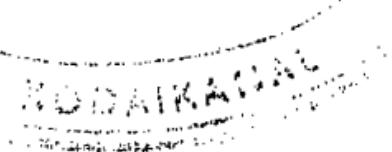
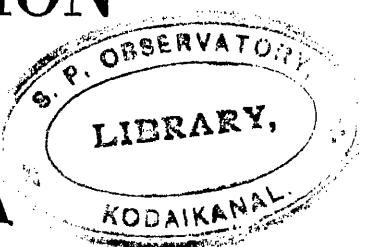


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The
INTERPRETATION
of
S P E C T R A



BY
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330 West Forty-second Street, New York 18, U.S.A.

1948

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Preface

The tables, which for convenience in reference, are collected at the end of the book, contain data not elsewhere available regarding intimate relationships between spectra emitted by supposedly entirely different sources.

That such accurate mathematical relationships occur was not expected by the current theory regarding the origins of spectral lines. These newly evaluated relationships must be taken into account by present-day theory or by any future theory dealing with the nature of light.

Chapters 2 to 7 explain in detail how the data set forth with mathematical precision in the tables were evaluated.

As the new relationships revealed by mathematically precise comparison of spectra from different sources appear to me irreconcilable with assumptions now quite commonly accepted, I have made a serious attempt to account for spectra without quantum assumptions or any other assumptions contrary to mechanical and electro-magnetic principles commonly used in engineering, as in the design of dynamo-electric machinery, transformers, cyclotrons, electron microscopes and communication by telephone or radio.

Chapters 8 to 14 present the results of these attempts to begin development of a theory of spectra that does not conflict with other theories which have proven of practical utility.

In the final chapter I have permitted myself to present some speculations about the structure of atomic nuclei, and the relationships of matter to the medium in which light is propagated, which may be of interest to the reader if he is inclined to speculate beyond the range of our present ability to test hypotheses by experiment.

The introductory chapter is intended to prepare the reader for consideration of the study of spectra from a new point of view. It contains a brief summary of my own work, treated in detail in other chapters, and of inferences that I have drawn which differ from assumptions of current theory, followed by a discussion of the premises of electromagnetic theory and certain inferences regarding the teaching of that theory which are made by quantum theorists and which I think are mistaken.

William Mayo Venable

Pittsburgh, Pa.,
March 31, 1947.

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Chapter 1

Introduction

About twenty-four years ago I had occasion to inquire as to what was known about the actual process of absorption of light. I soon found that although there was considerable practical knowledge of the effects of such absorption and of the conditions under which absorption takes place, much of which was of practical use, as in photography, nothing was really known about the process itself, or about the reverse process, the emission of light.

The most exact information available had been correlated in orderly manner by empirically discovered mathematical formulas, by which certain groups of spectral lines attributable to a common source were systematically arranged with respect to one another. These groups were attributed to chemical elements, or to molecules of chemical compounds, according to the sources from which they were obtained by heat or electrical excitation.

Of these groups the one in which the mathematical formula expressing the numerical relationships is simplest is known as the primary spectrum of hydrogen. The formulation by mathematical rule was by Balmer, in the year 1885. Extended, this classification provided the starting point for Bohr's theory of atomic structure, launched in 1913. Bohr attributed this group of lines to hydrogen atoms, not in combination with other hydrogen atoms or atoms of any other element; each atom was assumed to be capable of emitting any one of the lines of the entire group, upon suitable excitation.

Besides the group of lines called primary, hydrogen can be excited to emit several thousand other lines which were not classifiable by Bohr's scheme, as I found in 1923. These were collectively known as the "secondary" spectrum, as if they were of minor importance, and without any classification whatever attributed to "the molecule."

The normal molecule of hydrogen is composed of two atoms. It was not an unreasonable demand upon a theory of the structure of the atom, based upon study of spectra, that it account with some precision for at least some lines of the simplest of molecules, if the atoms themselves were fully accounted for by the mathematical theory. This demand has never been met. For ten years after the launching of Bohr's theory of the hydrogen atom almost no progress had been made either in accounting for the secondary lines mathematically, or in finding systematic relationships among these lines with respect to one another. When I became interested in this spectrum the only groups that had been arranged in order were known as Fulcher's bands. They were few in number and accounted for only a few

lines each, as related to one another by intensity and mode of excitation. Other scientists, however, were working upon the classification of the secondary spectrum and progress was being made, assuming that these lines were of origin entirely independent of the origins of the primary lines.

In 1923 I began to study this spectrum, but I did not begin with the assumption that they are not related to the primary system, but from the very outset sought for such connection, which eventually I found, but not in a manner as simple as I had at first thought might be probable.

Before this work was completed, but after I was sure that the primary and secondary lines are related in origin, it occurred to me that, since this relationship which was supposed to be impossible by current theory as I understood it, there might be connections of a similar kind between other spectra usually ascribed to altogether different atoms, and that atoms might be compounds of simpler atoms, analogous to chemical compounds but much more intimately and permanently bound together. These sub-atoms might be separated by suitable excitation and their parts recombined in configurations that are responsible for spectral lines, and not the chemical atoms themselves. Accordingly, I laid aside my work on hydrogen long enough to compare other spectra in a preliminary way. In 1933 I published a book entitled "The Sub-Atoms" which contained a substantially correct table showing the relationship of the primary and many-lined spectra of hydrogen. This is the first publication indicating the possibility of such a relationship of chemical atoms to one another, which I have more fully discussed in this book. More complete data relating to hydrogen was published by me in book form in 1942, but of this only two hundred copies were printed. The data there published, with some additions and corrections, are contained in Chapter 2 of the present work.

Chapters 3, 4, 5, 6 and 7 deal with comparison of spectra of supposedly entirely independent origin with one another and with the spectrum of hydrogen, and reveal correspondences which indicate common factors, presumably in the origins of the lines observed. They are interpreted as confirming the hypothesis that chemical atoms are complex, and as indicating the sub-atoms, of which several different chemical atoms are compounds. The relationships discussed in these chapters are *facts*, regardless of what interpretation may be placed upon them, and they should be of interest to all persons interested in spectroscopy from a mathematical point of view, and to all interested in atomic or nuclear structure. The data are collected for critical study by any persons interested, and are placed together at the end of the book. In the chapters discussing these tables I have not attempted to justify the scheme presented as a physical theory, but to present the facts as clearly as I can, leaving theory to be discussed after the *facts*, which I think are *important*, and which have never been taken into consideration. They are established and so presented that any person interested in atomic structure may give them any interpretation which seems to him tenable.

Since I use the classification data provided by others, and examine them with a view to a different interpretation as to the causes of the regularities disclosed, it is desirable that I preface that use with some remarks as to the manner in which these data were acquired.

Classification of spectral lines by means of mathematical formulas was not begun until a great deal of classification of quite another kind had been accomplished. The initial classifications were altogether empirical. By comparison of spectra emitted upon excitation of different substances, it was found that the presence of certain chemical elements in the source resulted in the emission of certain lines not otherwise present. The position of each observed line in the spectrum could be measured and the "wave length" calculated. Thus certain groups of lines were associated with the presence of certain chemical elements. This identification of lines and groups of lines with chemical elements was established before there was any theory as to how the lines are emitted or how they are related to one another either mechanically or mathematically. Fundamentally, this kind of classification is that used in chemical analysis by spectroscopic methods, although in the development of the science of such analysis various methods of excitation capable of revealing certain relationships have been developed to supplement the mere identification of lines by wave length.

Certain regularities in the spacing of lines assigned to the same source are evident upon inspection of spectra. Thus the series of lines known as the Balmer series of hydrogen is almost unavoidably apparent when those lines appear on a photographic plate practically alone. This particular regularity was reduced to mathematical rule by Balmer in 1885; and shortly thereafter a more general formula, the Rydberg formula, was found to include the Balmer series and several other series of similar kind. This was in 1890. Twenty-three years later Bohr proposed his model of the hydrogen atom to account for this formula on the assumption that hydrogen atoms, not in combination with one another in any way, were responsible for all the lines accounted for mathematically by the simple Rydberg formula, to a first approximation. In doing this he assumed the existence of dynamically "stable states" in atoms, which was contrary to the principles of electromagnetic theory. The Rydberg formula is a mathematical guide of great utility in classification. It does not depend upon whether or not the lines are emitted by atoms or molecules. Bohr regarded his assumptions as justified by their consistency with one another, and particularly by the fact that by applying his various assumptions he was able to devise a formula giving the relation of the Rydberg number to Planck's constant and the known charge of the electron. Bohr's formula is a statement of fact, approximately accurate; but it does not prove the various assumptions which he found useful in deriving it, or at least in presenting it in his theory of structure of the hydrogen atom, because the same formula may be quite consistent with some other assumptions.

Discovery of other mathematical formulas did not await Bohr's formula.

Modifications of the Rydberg formula were made empirically, and modified formulas were found that classified other groups of lines, attributed to other elements, quite satisfactory for preliminary purposes. A summary of the work of classification accomplished up to that time was made in Fowler's "Report on Series in Line Spectra" in 1922. That report records both lines and levels (calculated) of well defined, fairly regular first order series, with a short account of the second order, or regular spectrum of helium. Those first order series, all fairly long, are produced by elements of large atomic volume. Their classification antedated the development of the scheme now in general use for the preliminary classification of more complex spectra, which also was discovered by trial, but is claimed by wave mechanics as a product of theoretical inquiry.

The theory of wave mechanics retains the essential assumption of Bohr, that atoms emit "quanta" of radiation, now called "photons," which are monochromatic, and each endowed with a fixed amount of energy equal to its frequency multiplied by Planck's constant. These photons are supposed to move only with the velocity of light, not subject to acceleration or retardation, but are otherwise like particles of matter. All that I wish to insist upon here is that it is quite legitimate to use the formulas which actually are found to accord with observation, if not actually derived from it, without assuming the philosophical interpretations by which wave mechanics justifies them in view of its theory, which denies the validity of electromagnetic theory in the domain of atomic physics. "Energy states" are expressed with precision in terms of wave numbers, and wave numbers mean frequencies. I shall make free use of wave numbers of levels as expressing what we call frequencies, and leave their interpretation to follow in the theoretical treatment of the chapters in the latter portion of this book. All mathematical rules and formulas that have been found helpful in classification, including those of Planck and Bohr, will be regarded as data. No hypotheses will be regarded as data.

The task of accounting for the structure of atoms or other bodies that can account for spectra is not completely accomplished by consideration of data derived from analysis of spectra alone, or by the comparison of spectra from different sources. The results of study of mass spectra and of "atom smashing" experiments must also be taken into account before the structures of atoms can be fully delineated. If atomic nuclei are in fact compounds, they may be broken into component parts without altering any of the nuclear sub-atoms appreciably.

The analyses and comparisons of systems of spectral lines discussed in the first seven chapters of this book reveal relationships of spectra from supposedly entirely different sources, which either were entirely unknown to the founders of the theories now in general use to account for spectra, or were overlooked, or assumed to be impossible. In the second part of the book, beginning with Chapter 8, I shall endeavor to account for them as well as for the better known facts regarding classification and analysis in a

manner consistent not only with the observations but also with the principles employed in mechanical and electrical engineering, some of which are either ignored or rejected by the theory of quanta including its more recent form, wave mechanics.

The subject is so vast, and its details so complicated, and in certain parts of the field the experimental data are so meager and obviously lacking in accuracy, that I cannot hope to do more than make a beginning in developing a treatment from a hitherto neglected point of view. Before attempting even this I shall briefly summarize the facts that are revealed by the analyses that are new, and require to be taken into account, divesting them of the adornment of hypotheses which I have found convenient to use in showing the hitherto neglected mathematical relationships of spectra from different chemical sources.

(1) The use of the primary levels of hydrogen is necessary for the complete analysis of the many-lined spectrum. Without investigation this has been assumed by quantum theorists to be untrue.

(2) A very much smaller number of levels is required to account for the entire spectrum of hydrogen if the numerous lines are regarded as compounded of pairs of differences between levels than as simple differences between individual levels, as is the current practice.

(3) The same difference numbers assignable to pairs of levels recur many times in spectrum analysis of different separately classifiable band systems and sub-systems, revealing hitherto unknown relationships between such sub-systems.

(4) Differences evaluated by analysis of the many-lined spectrum of hydrogen were found repeated as differences between levels in the spectra of helium, including both those of line spectra and those of band spectra.

(5) Some of the same differences recur between levels of helium and levels of lithium.

(6) A rather large number of the same differences recur between corresponding levels of neon belonging to different series.

(7) A considerable number of the same differences evaluated by analysis of the hydrogen spectrum recur as differences between doublets in first order spectra of other elements.

(8) Both K and L x-ray spectral lines may be accounted for as due to deductive compounding of differences between "Lyman" lines of atoms of different atomic number.

These itemized statements require no more complicated methods for their verification than the simple process of arithmetical subtraction. They are facts, absolutely indisputable, regardless of what interpretation may be placed upon them. They may be ignored but not disproved. The following additional facts are obtained by comparison of quantum numbers, which are obtained with the assistance of series formulas acceptable to current theory, but obtainable by mathematical analysis without any theory, empirically, from the observed spectral lines.

(9) Modified series formulas of the Rydberg-Ritz type are capable of accounting for all the levels that must be assigned to hydrogen spectra as classified by analysis.

(10) From the wave number of the first Balmer line of hydrogen and that of the corresponding line of deuterium, by the use of formulas patterned after those used in the classification of hydrogen lines, thirty unknown possible lines that might occur in mixtures of hydrogen and deuterium were calculated, and thereafter found in photographic records of the spectrum of mixtures of hydrogen and deuterium.

(11) Some of the levels of helium and lithium could be accounted for in a similar manner as due to levels which might result from modifications of second order helium levels by accretions of hydrogen atoms to the molecules responsible for the regularly progressing helium levels.

(12) Intimate relationships of a similar kind were found between helium levels and those of lithium and several other elements of small atomic number.

Independently of these numerical relationships, there are other indications that atoms are of composite origin, of which the most important are:

(13) Hydrogen primary lines always are excited during the excitation of pure chemical elements which emit long first order series. These lines are most prominent when the excitation is initiated. As the spectrum develops more and more terms, the hydrogen lines diminish in intensity, but seldom if ever disappear entirely.

(14) Those elements which yield long first order spectra or numerous series of well defined first order spectra also are those of large atomic volume.

(15) Continuous spectra always accompany the emission of spectral lines. The most intense portion of these continuous spectra is not usually in the same portion of the spectrum as the more numerous lines; but frequently, especially when the gas pressure is high and the excitation has not been long continued, the continuous spectrum is sufficiently intense in the regions of lines to obscure many of those of small intensity. In hydrogen and helium the continuous spectrum is more intense in the far ultraviolet than in the visible region of the spectrum; and as the excitation is prolonged and the pressure reduced it apparently withdraws in intensity toward the region of higher frequency, or shorter wave length, but does not disappear altogether if looked for in the proper region.

(16) The characteristic continuous spectra do not, however, depend upon the excitation voltage for their upper limit providing that voltage exceeds the required voltage for excitation of all spectral lines. Each has a definite upper limit which has been ascertained for hydrogen and is given in the analysis of the hydrogen spectrum.

Of course, in addition to these facts which seem to me to have been unknown or overlooked hitherto in accounting for spectral lines, other facts must be taken into account in any theory which will account for spectral lines in an adequate manner. These facts include all that is known about

classifications made by the usual methods, whether guided by philosophical theories or merely mathematical formulas or rules found applicable by experience. All such facts, including the formulas and rules, constitute data. I do not regard philosophical interpretations as data, and shall not consciously use any assumptions that seem to me to contradict the ordinary principles of mechanics and electromagnetics employed in the various branches of electrical engineering, including electronics.

In a theoretical inquiry regarding such a matter as the origins of spectra it is necessary to employ hypotheses in order that they may be tested. They must be discarded or modified if found inconsistent with data. I have employed such hypotheses, and have been obliged to modify some of them in the progress of the inquiry. Those which I propose as suggested by the data uncovered in the chapters of the first part of this book are as follows:

(a) The many-lined spectrum of hydrogen is not entirely independent of the primary in its origin. Whatever the sources of the primary lines, the same sources also contribute to the development of the many-lined spectrum, but with the cooperation of other sources, whatever they may be. This is basic, and is in outright conflict with the current opinion.

(b) The simple differences evaluated by analysis of the many-lined spectrum of hydrogen cooperatively combine to produce the wave numbers of the numerous lines. Therefore, accounting for these differences and not for the lines themselves is the first step required in explaining the spectral lines themselves.

(c) It is most probable (there may be exceptions) that these differences arise from differences of frequencies characteristic of different molecules, which interact with one another by processes of absorption or accretion, the degree of such interaction depending to some extent upon proximity. The great multiplicity of lines is then due to the multiplicity of the different types of molecules involved, but is very much greater than the multiplicity of the varieties of molecules required.

(d) The differences found by analysis of the hydrogen spectrum and attributed to molecules composed entirely of hydrogen, but which also occur as differences independently evaluated in the spectra of other elements are due to the same molecules in both cases. This involves admission of one of two alternatives. Either hydrogen is present as an impurity in the excitation chamber where the other spectra are observed, or it is liberated from the atoms of the other element by the process of excitation. All the evidence points to the latter alternative in the cases of atoms of large atomic volume, and to the former in those of very small atomic volume.

(e) Atoms of higher atomic number than 1 are composite and contain within their structures (or compounded nuclei) one or more sub-atoms of less atomic number than that assigned to the chemical atom as a whole.

(f) Under excitation atoms may be separated into component sub-atoms, with losses of electrons during the process of subdivision. These sub-atoms

recombine with one another to produce the molecules cooperatively responsible for the observed spectral lines.

This hypothesis has far-reaching postulates, derived from the nature of the structure of the spectra actually observed. One of these is that those sub-atoms which combine linearly to produce lines or levels are accompanied by only one electron each. This is a condition which will be found necessary in the theoretical treatment, and was not anticipated *a priori*.

Another postulate related to this one is that, if there are partially ionized sub-atoms with more than one electron accompanying them, they may contribute to continuous spectra, but not to line spectra. Both of these postulates need not be discussed here. They are mentioned in order that the reader may not think that they have not been taken into consideration in connection with the scheme now being developed.

(g) What is known as the atomic number of a chemical element is the largest atomic number of any of its constituent sub-atoms.

(h) Series formulas, when the progressions are regular, reveal levels in some manner to be ascertained but not known *a priori*, due to accretions of like sub-atoms of one configuration only to initial simpler molecular combinations. When the progressions are erratic, or irregular, the formulas do not reveal the true levels, but their wave numbers depart from the true levels by accretions from other sources.

This hypothesis is necessitated by discovery of hydrogen and other differences between levels of one series and those of another, independently evaluated by lines supposed to have an upper level in common. Recognition of the principle stated in this postulate is necessary for the further interpretation of most of the spectra now not completely classified.

The last few postulates stated are formidable, but cannot be sidestepped by theory, though accounting for them imposes stringent conditions upon the type of nuclear structure that must be found to account for all spectra in a consistent and orderly manner. The structures also must be consistent with mechanical and electromagnetic principles, and must account for all types of continuous spectra as well as for line spectra.

These hypotheses also modify very materially the expectations as to the number of enhanced spectra that should be expected of different chemical elements, as that must depend upon the number of different varieties of sub-atoms in the atomic structure and not upon the number of electrons assignable to the highest atomic number only.

Since hydrogen is supposed to be the lightest chemical element, and certainly is the lightest that yields a line spectrum, interpretation of line spectra ought to begin with those of hydrogen. This will be attempted in Chapters 10 to 14; but since I intend to make this interpretation without departure from any well established electromagnetic principles, and since the current theories not only make such departures, but justify them by arguments, it seems pertinent as a preliminary to other discussions to make brief mention of the electromagnetic theory of light.

In elementary treatises dealing with certain phenomena, such as interference, it is very convenient to consider spectral lines as though they were made up of wave trains in which all waves are alike and, at least for a first approximation, simple harmonic. This, however, is not in accord with electromagnetic theory, nor is it verified by experiment. The electromagnetic theory and the wave theory as thus presented are not identical.

A wave theory of light was developed before and quite independently of the electromagnetic theory. Originally it had no connection with electrical science. That many, if not all forms of light might be attributed to trains of waves was believed before the velocity of light was known to be the same as the velocity of the electromagnetic pulses which account for transmission of energy. The discovery that this velocity is practically the same for light as for other forms of electromagnetic induction was the first truly scientific link between the wave theory of light and electrical engineering.

On the other hand, the electromagnetic theory, though it came later than wave theory of light, was not based upon that theory, nor is it a theory that deals primarily with trains of waves. It interprets individual electromagnetic pulses, and in so far as it discusses wave trains it regards them as successions of pulses. The individual pulse is interpreted, and all the phenomena to be considered must be traced to the behavior of individual pulses.

For many practical purposes, however, it is convenient to employ trains of similar pulses following one another in regular sequence, at equal or approximately equal intervals of time. Such pulses collectively constitute wave trains, and they may be so arranged that they may act in a similar manner and cooperatively perform useful work. For example, an alternating current generator, running at constant speed, may develop a form of energy which can be transmitted to a distance, guided by conducting wires, and operate an alternating current motor, in synchronism with the generator. This kind of transmission employs the principle of resonance, each successive pulse or pair of pulses of opposite direction acting upon the motor in the same manner as others. It is, however, quite possible to devise a motor which can be operated by a constant speed alternating generator, but with variable speed at the motor. In each case the successive pulses are made to do useful work; but to design the machines it is necessary for the engineer to understand the action of the pulses and not to be limited by a partial understanding of the continually acting succession of pulses.

Very much the same thing is true of the pulses which are popularly known as radio, which do not require wires for their guidance. The pulses may be of either constant or variable frequency. In both cases, the apparatus must be designed to produce the desired regularity or variability, and to make use of it at the receiving end.

In discussing various phenomena of light it is usual to overlook the individual pulses and to consider only wave trains of constant frequency — but only in certain instances, and where the discussion is somewhat super-

ficial. Thus phenomena of interference are easily understood as due to superposition of waves having the same frequency but differing in phase. If the nature of the individual pulses is ignored, this kind of treatment is merely the old wave theory of light, and not electromagnetic theory at all.

Light is now considered as due to the behavior of electrons impinging upon or associated with atoms. But when the electromagnetic theory was formulated there was no knowledge that the electron could be separated from the atom or molecule, and studied as an individual particle, moving in a vacuum under the influence of electrical and magnetic fields. A unit of charge equal to that of the electron was known from electrochemical measurements, but that this charge was associated with a unit of mass was unknown. Therefore, before J. J. Thomson's discovery in 1897, the electron was not under investigation as a source of light. But it was known that light and heat were intimately related, although the mechanism by which radiation occurs was altogether unknown. A body heated above the temperature of its surroundings not only communicates heat to any body in contact with it, but also radiates heat to distant bodies. When the temperature is raised sufficiently this heat is sensible to us not only as heat but also as light; and as the temperature is increased the color sensation produced by the light also changes. It was definitely known that the total energy radiated as heat and light is proportional to the fourth power of the absolute temperature.

The distribution of the heat in the spectrum of a body radiating because of temperature only was studied experimentally; attempts were made to account for this distribution, without knowledge of the mechanism by which it takes place, by the application of principles of the theory of thermodynamics, assisted by various assumptions. One of the arbitrary assumptions that played a very important part in these theoretical studies was that light consists essentially of monochromatic wave trains, and not of individual pulses. Among those who were very prominent in those theoretical, or rather mathematical inquiries, were Wien (1896), Thiessen (1900), Rayleigh (1900) and Jeans (1905). Their attempts were not successful, but in 1900 Max Planck succeeded in modifying proposed formulas in a manner that gave results in close conformity with the results of observation.

Planck's first publication was in 1901. He lectured in Berlin on the theory of heat radiation during the years 1906-7 and published those lectures in book form. Another edition was published in German in 1912. This was translated into English by Masius and published in 1914, at which time the existence of the electron was well known.

Planck, like the others, treated light as consisting of minute monochromatic wave trains, but he justified this on the ground that for purposes of computation this treatment is sound, because, though light may actually occur in completely heterogeneous pulses, each pulse can be treated mathematically as equivalent to an infinite series of monochromatic wave trains

of determinable distribution. This treatment is purely formal, and does not imply that the pulses actually are physically resolvable by optical instruments into such wave trains. He made no assumptions conflicting with electromagnetic theory. However, after the work of Thomson was known, both Einstein and Bohr made assumptions that were well known to be in conflict with electromagnetic theory, which later came into wide acceptance in the interpretation of spectra. At the time of publication of his second edition in 1912 Planck did not accept these additional assumptions, as will be clearly evident from the following passages quoted from the English translation. In the preface Planck states:

"While many physicists, through conservatism, reject the ideas developed by me, or, at any rate, maintain an expectant attitude, a few authors have attacked them for the opposite reason, namely, as being inadequate, and have felt compelled to supplement them by assumptions of a still more radical nature, for example, *by the assumption that any radiant energy whatever, even though it travel freely in a vacuum, consists of indivisible quanta or cells.* Since nothing probably is a greater drawback to the successful development of a new hypothesis than overstepping its boundaries, *I have always stood for making as close connection between the hypothesis of quanta and the classical dynamics as possible,* and for not stepping outside of the boundaries of the latter until the experimental facts leave no other course open." And again on page 108:

"In fact, black radiation may just as well be regarded as consisting, *not of regular periodic vibrations, but of absolutely irregular impulses.*"

The course which I shall follow in succeeding chapters is identical with this recommendation of Planck. He did use a supplementary assumption as a mathematical expedient, but he did so recognizing that it was an expedient only, and he did not depart from electromagnetic theory even in this assumption. I shall endeavor to use no hypothesis in conflict with the principles of mechanics or of electromagnetic theory applicable in electrical engineering. I shall assume that electrons within atoms obey the same laws as they are known to obey elsewhere.

Remembering that the electromagnetic theory interpreted electromagnetic pulses, and considered wave trains as due to the apparatus in which the pulses were produced, after the discovery of the electron as a particle the natural expectation should have been to account for light as due to pulses resulting from accelerations and retardations of electrons associated with other particles of matter. From this point of view the problem is: "What can be the structure of matter that would occasion pulses and sequences of pulses that can account for the distribution of energy in the spectra that is actually observed, and what can be the manner in which spectral lines of approximately constant frequency, as defined by the wave theory of light, are produced?" This is the problem that now confronts us.

But this problem was not attacked, or even stated, shortly after the discovery of the electron as a particle which might produce pulses. Instead

of attacking the problem on the basis of the soundness of our engineering knowledge of the behavior of charges, which would require use of the electromagnetic theory, various assumptions known to be discordant with the electromagnetic theory were introduced, and it was alleged that electromagnetic principles cannot be applied to phenomena of the origin of spectra. Because these assumptions must now be either modified or set aside altogether, and also because they are intimately associated with the formal schemes in common use in the classification of spectral lines and their interpretation, I shall list some of them in approximately the order in which they were introduced, and point out wherein they are either aids or hindrances in advancing to a more rational understanding of the relationships between atomic structure and light.

(1) *Atoms known to the chemist are individually the origins of characteristic spectral lines.* This hypothesis was tacitly and generally assumed after it was found that certain groups of lines are produced by excitation of certain elements. It was natural because there was then no known evidence that atoms may be divisible under the conditions of excitation. Quantum theory and wave mechanics adopted it without inquiry.

(2) *Each atom in the neutral state consists of a single relatively massive nucleus with a positive charge, about which negative electrons sufficient in number to neutralize the positive charge are in equilibrium.* This idea, with the proviso that both mass and charge are concentrated in a very small space about the atomic center, was introduced by Rutherford about 1911, to account for the scattering of alpha particles from radium passing through thin sheets of metal, as due to repulsion between the alpha particles and the positive nuclei. That the atomic nucleus is not divisible is not tenable in view of the facts derived from comparison of spectra discussed in Chapters 2 to 7. There are other types of nuclear structure that will satisfy the scattering observations as well as that assumed by Rutherford.

(3) *The stability of the electrons about the nucleus is dynamic.* This assumption also originated with Rutherford. It was adopted by Bohr as the basis of his model of the hydrogen atom — the first step in the modern theory of quantum structure of atoms, and of the emission of line spectra. This hypothesis is not tenable now for either an atom as a whole or for the sub-atoms of which its nucleus is composed, because:

(a) Dynamic equilibrium of an electron is contrary to well known electromagnetic laws, which have been proved by the experiments of Thomson and others to apply to electrons as particles moving freely *in vacuo* in electric and magnetic fields.

(b) Such motion is incompatible with the maintenance of stability in chemical compounds and crystal structures known to the chemist and the physicist, in which both electrons and ions are poised in ascertainable relationships or geometrical patterns, though subject to minor deflections and restricted motions about positions of stability.

(c) Orbital motion of electrons also is incompatible with both the duplication and the shifting of x-ray lines upon reflection, as observed in the Compton effect.

(4) *All first order spectral lines are emitted by neutral atoms or molecules. They are not the result of cooperation of different sources.* This is pure assumption, and is tacitly accepted by Bohr's theory. His theory of the origin of the primary spectrum of hydrogen is based upon it. That this cannot be universally true is evident from the following considerations.

(a) Light of a spectral line from one element passing through a medium composed of another element may give rise to a number of other lines which differ in frequency from the original line by frequencies characteristic of the element in the medium. This is known as the Raman effect. This effect was not known when Bohr formulated his theory.

(b) A spectral line from an element high in the scale of atomic number, in the x-ray region, may be modified by reflection from an element of lower atomic number. This is known as the Compton effect.

(c) In Chapter 2 I have shown that the primary spectrum is also a contributor to the many-lined spectrum of hydrogen. This is contrary to the postulate of Bohr's theory that the primary spectrum originates in atoms exclusively and the secondary spectrum in molecules. If atoms and molecules both contribute, they cooperate in the production of spectral lines. This cooperation is not the same as the Raman effect as ordinarily considered, because the "combinations" are between "levels" and not exclusively between lines.

As applied to the hydrogen spectrum, Bohr's assumption overlooks the fact that hydrogen atoms, after liberation from either of the two normal molecular forms now known to exist, may combine into new molecular forms of somewhat different character from the normally stable ones.

(5) *Singly ionized atoms emit second order spectral lines.* This was assumed by Bohr to account for the regular spectrum of helium in harmony with his theory accounting for the primary spectrum of hydrogen.

This assumption probably is partially true for the sub-atoms of which atoms are composed, but not for atoms as wholes. The analysis of the helium spectrum discussed in Chapter 4 indicates that the regular spectrum of helium originates in molecular combinations of singly ionized atoms of sub 2. The ion alone thus has charge $+e$, and a combination of two such ions a charge $+2e$. The spectrum assigned by current theory to the normal helium atom, however, according to the analysis of Chapter 4, is not due to neutral atoms, but to combinations of singly ionized atoms of sub 2 with neutral hydrogen atoms, in various molecular configurations.

(6) *Singly ionized atoms also are responsible for x-ray spectral lines.* This is not based on Bohr's original scheme, which ascribed successive orders of spectra to successive losses of electrons, but on a modified scheme to account for x-ray spectral lines only. This scheme assumes that without ejection of an external electron an electron may be ejected from an "inner shell" of an

atom of sufficiently large atomic number, producing an ion of charge $+e$, and the inner electron replaced by another from an outer shell, with the production of an x-ray line. The scheme is highly artificial. The levels must all be calculated from observed x-ray lines, and are not predictable from the general principles upon which the theory of the hydrogen was based. As a scheme, it is consistent, and has been very useful in classification of x-ray lines. It is not compatible with the scheme outlined in Chapter 7, which has, I think, better mathematical justification.

(7) *The number of different orders of spectra that an atom may emit is equal to its atomic number.* (According to the Bohr-Rutherford scheme, this is equal to the number of electrons surrounding the positive nucleus in the neutral atom.) This is another assumption that is purely schematic. It is not necessarily sound if the atom is in fact a compound made up of a number of simpler sub-atoms; and it is not wholly in keeping with the fact that there are many groups of spectral lines now assigned to the same degree of ionization, but not as yet correlated by known combinations of levels. It is an assertion based upon hope, not upon accomplishment. Some remarks regarding this have been included in Chapter 6.

Nevertheless, this hypothesis is a useful guide in extending classifications of spectra not yet accomplished.

The seven assumptions just listed relate to facts which should be verifiable or capable of disproof. Even if we leave altogether out of consideration whether or not they are antagonistic to the electromagnetic theory, which is our most reliable guide in all branches of electrical engineering, we still are confronted with the fact that they are not reconciled with ascertained relationships between spectra assigned by the parent theory to entirely different origins. Moreover, they are only assumptions of a general nature, and many other assumptions of a more specific kind are encountered in application of wave mechanical principles to observations. By way of example of a supplementary hypothesis consider the invention of the term "metastable state" to account for the offset levels first found by Paschen in analysis of the spectrum of neon. These were not anticipated by theory, but were discovered by the most painstaking analysis. Thereafter, they were included in the "scheme," a place being made for them and a terminology invented.

The present scheme has well coordinated rules for determining differences between levels that are likely to produce observable lines, which involve "combination principles" and "selection rules"; but these rules are so frequently broken that one must consider the exceptions as important as the rules, when we attempt to formulate a physical theory, not merely a scheme, to account for them.

The abler advocates of wave mechanics insist that electromagnetic theory is wholly incompetent to account for spectra, and that there is no alternative but quantum theory. The chief arguments advanced against the electromagnetic theory are:

(1) It insists that spectra must in the last analysis be attributed to pulses. A pulse is the mathematical equivalent of an infinite series of monochromatic wave trains, into which it may be resolved, mathematically, by Fourier series. According to such analysis there should be no limit to the spectrum due to any single pulse, on the short wave length end, and there are no actual spectra which do not reveal such limits. In particular, they are observed in

(a) Black body radiation due to temperature only, in which the short wave length is fixed by the temperature.

(b) Continuous spectra produced by electron bombardment (chiefly in the x-ray regions) where the short wave length limit is fixed by the excitation voltage.

(c) Characteristic continuous spectra in which the short wave length limit is fixed by the atomic number of the element bombarded. That elements generally have characteristic continuous spectra has not generally been recognized. Probably this is due to the fact that in the x-ray region such limits are overlapped by the non-characteristic spectra due to the bombardment potential.

(2) Electromagnetic theory cannot account for the Compton effect, observed when an x-ray spectral line emitted by an element of large atomic number is reflected by an element of smaller atomic number. A single line is reflected as two lines instead of one; one of the reflected lines is of the same "wave length" indicated by its position on the observer's scale, while the other has a greater wave length, the difference between the two depending upon the angle of reflection and also upon the atomic numbers of the two elements concerned.

If light consists primarily of pulses, it is to the character of all individual pulses, and not to monochromatic wave trains, that we must look for an interpretation of continuous spectra and the Compton effect. The latter are discussed in the chapter on excitation.

Although in the chapters to follow I shall endeavor to throw some light upon the subject of nuclear structure of the sub-atoms present in normally stable atoms, I make no attempt to account for the abnormal or unstable forms of sub-atoms which must be present in unstable atoms produced as results of "atom-smashing" experiments, or to account for the energy liberated when such changes occur or which must be supplied to initiate them. We have no data about line spectra emitted by unstable atoms. Such atoms are not produced unmixed with other atoms under conditions that as yet make such investigations practicable. The hypothesis that atoms are complex, that is, composed of sub-atoms, has this bearing upon the interpretation of the results of atom-smashing experiments: the nuclear changes must be ascribed to the sub-atoms, instead of to the atoms as wholes. Some remarks upon how this would affect the interpretation of the observed final products of atom smashing or of fission are given in the last chapter.

It is now well known that nuclear changes produced artificially or as a result of cosmic rays often are accompanied by the emission of electrons, either positive or negative, with very high velocities, as determined by their deflections in very intense magnetic fields. The electromagnetic theory would expect these emissions to be accompanied by very intense electromagnetic pulses — single pulses, not wave trains. These pulses would not necessarily, on *a priori* grounds, be expected to have the same energy distribution as the pulses produced by electrons impinging upon ions from without. In fact, the probability is that they are of quite different character. The analyses which I have made do not deal with these at all.

Chapter 2

Classification of the Lines of the Spectrum of Hydrogen

Any student of spectroscopy learns that under suitable conditions of ion hydrogen emits a group of lines which may be classified by the Rydberg formula. Some of these lines are also emitted by excitation nical compounds containing hydrogen and some of them accompany spectra attributed to other elements, and are used as secondary standar the measurement of lines of other spectral groups.

It is not generally known, even to those who are professional spectroscopists dealing chiefly with chemical analysis, that pure hydrogen may also emit several thousand lines which are not classified by the Rydberg formula. These numerous lines are referred to at all in elementary text books and are called "secondary," as though of minor importance, which is very much being true. The easily classified and identified lines are called "primary." It is with the classification of the numerous lines, and their relationship to the primary lines that this chapter is concerned.

All show that the numerous lines are related to one another and to the primary in a manner which indicates community of origin. Possibility of this relationship is not anticipated by the theory of origin of spectral lines now in general use, which attributes the primary lines to atoms and the numerous other lines to molecules. The connections between the primary system and the numerous sub-systems of the many lined spectrum could not be known at the time the current theory was launched in 1913 because at that time nothing was known about the classification of the numerous lines.

Many workers have contributed to the measurement and correlation of lines into groups independently classified, although the relationship up to group was unknown. The first step necessary was accurate measurement of the lines followed by calculation of their wave numbers and the wave lengths measured.

There are two long lists of lines available to those who desire to attempt classification. The first of these is that of Merton and Barratt, published in the Royal Society April 27, 1922. It contains wave lengths and wave numbers of more than 1300 lines, with much information relating to the causes of variations of pressure and mode of excitation upon the relative intensities of individual lines. The second list is that of Gale, Monk and

Lee, published in the *Astrophysical Journal* of March 1928. This list contains wave lengths and wave numbers of 3025 lines, more precisely measured than those of Merton and Barratt, because of improvement in spectroscopic equipment. Gale's list, however, does not give information about changes in excitation, and both lists are necessary if one desires to do classification work in this field. Besides these published lists Professor Dieke at Johns Hopkins has an even more comprehensive list, which has not yet been published. I used Gale's wave numbers in my work after they became available, and in the tables assembled at the end of this book, except for the bands classified by Dieke, for which I have used his wave numbers as published.

A little preliminary work of classification had been done before the publication of Merton's tables. Shortly after Merton's tables were available, Richardson and his co-workers attacked the problem of classification systematically and made more than twenty progress reports, which were published by the Royal Society from 1924 to 1933 inclusive. Professor Richardson kindly sent me reprints of all these papers as they became available. He summarized this work and his interpretation of its results in his book entitled "Molecular Hydrogen and Its Spectrum," published in 1934.

My own work on the hydrogen spectrum began in 1924. From the start I sought connections between the primary system and the independently classifiable groups of the many lined spectrum, and followed methods different from those followed by others. However, I had the benefit of the work of others and made use of their published classifications without modification, except in those instances where I did not think the published classifications were correct. In a few cases I have made changes which I have explained in the text of this chapter, and I have added a few sub-systems of my own discovery.

My contribution to the analysis of the hydrogen spectrum consists chiefly in finding the relationships of various sub-systems properly classified into systems by others to one another and to the so-called primary system, which now is shown to be a special sub-system of a comprehensive general system by which all of the lines are related to one another. The relationships thus disclosed make a different interpretation of the sources of these lines from that in common use imperative; but the results of having discovered these relationships are much more far-reaching than that, for it will be shown in chapters to follow that hydrogen contributes to the development of spectra of other chemical elements, in ways not hitherto recognized.

Classification of lines by series relationships of wave lengths began with the work of Balmer, correlating the lines known as the Balmer series of hydrogen. His formula was soon converted into one expressing the same relationships in terms of wave numbers, the reciprocals of wave lengths, *in vacuo*, thus becoming

$$\nu = 109678 \left(\frac{1}{2^2} - \frac{1}{n^2} \right)$$

in which ν is the wave number of a line and n an integer greater than 2.

The next step was to include in this classification other series of lines, the wave numbers of which are given by the more general formula

$$\nu = 109678 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

in which n_1 and n_2 are whole numbers. If $n_1 = 1$ the lines belong to the Lyman series; if $n_1 = 2$ the lines belong to the Balmer series; if $n_1 = 3$ they belong to the Paschen series, and so on. Thus, mathematically, every line may be regarded as having a frequency that is a difference between two other frequencies at which no lines are found. These no-line frequencies are called levels.

The number of "levels" necessary to account for the primary spectrum of hydrogen is much less than the number of lines to be accounted for. Thus it is a simplification of the problem of classification of spectra to proceed by determining the levels, and to regard the lines as differences between levels. This practice has been followed in classifying other spectra, even the most complicated. The series formulas by which these levels are related are not as simple as the Rydberg formulas, but they may be found by search of the relationships of the spectral lines observed, though the actual progressions from "level" to "level" do not conform as closely to the mathematical formulas devised as do the lines of the primary spectrum of hydrogen. There always are discrepancies between mathematical formulas proposed and the wave numbers of the lines as obtained from wavelength measurements, though the discrepancies in many cases are very small.

But when we interpret the spectra we must not overlook the fact that the lines are observed, and not the levels. The levels are calculated from observed relationships of lines. In very many instances, if not in all, we may regard levels as differences instead of regarding lines as differences. Thus the Balmer level may just as well be regarded as the difference between the first and the second Lyman lines as the first Lyman line may be regarded as a difference between the Lyman level and the Balmer level.

In this and the succeeding chapters which deal with classification of spectra I shall follow the usual custom of treating lines as differences between levels, thus being able to use the classification work of others in the form in which it has been published. I shall, however, discuss the differences between levels from a new point of view, which is that in most cases lines are not simple differences between levels, but are compounded of several simple differences between levels, in an ascertainable manner which reveals the fact that a very much smaller number of levels is required to account for the entire spectrum of hydrogen than is required by the usual method of analysis. This leads to an entirely different interpretation of the origins of spectral lines from that now commonly held.

In this chapter and those which immediately follow, which deal with the spectra of other chemical elements, all classification is made by comparison with the levels of the primary spectrum of hydrogen, assuming the Rydberg number for hydrogen as 109678. The lines and levels to which we shall have most occasion for reference are given in Table 2 (p. 141). For convenience in reference, all tables which deal with the hydrogen spectrum are collected at the end of this book, and are numbered consecutively from 1 to 47.

The levels computed by assuming that the Rydberg number is a constant for hydrogen and that the simple formula is correct are given in both Table 2 and Table 1. It is known that the simple formula is not absolutely correct, but the error introduced by the assumption that it is so is too small to interfere with our use of these levels for the purpose of classification of other levels. For instance, the most accurate determination of the first Balmer line wave number is 15233.094, which would give for the Lyman limit, applying the simple formula, 109678.27 and for the Balmer limit 27419.55. The discrepancy between 15233.094 and the wave number I have used for the first Balmer line is only 0.034. It must be borne in mind, however, that when it comes to comparison of very small differences, such discrepancies do interfere with certainty of classification, and that when lines in the ultra-violet and Schumann regions are to be compared, the uncertainty of the observations is much greater than this. Thus there are practical limits to the extent to which classifications by means of small differences may be carried.

The number of primary lines that have been observed in hydrogen is very much greater than indicated in Tables 2 or 1. In stellar spectra as many as thirty or more Balmer lines have been observed. In the laboratory under the most favorable conditions, when the secondary lines are practically absent, as many as twenty Balmer lines have been measured; but when the secondary, or many lined spectrum is strongly developed, only six or seven Balmer lines are observable. Therefore in Table 1 all the other lines are compared with the first six primary levels, and of these only the first four or five are of great importance in outlining the general classification of hydrogen levels, in so far as it has yet been accomplished.

I shall now proceed to show that the origins of all the bands which have yet been classified in the spectrum of hydrogen, and many of the first band lines, may all be accounted for with precision as great as the accuracy of the measurements warrants, as due to the compounding of differences between levels assembled in Table 1 of this chapter, and then to show that these levels are related to one another mathematically in a significant manner, which reveals the relationship between primary and secondary levels. In other words, "combinations" between primary and secondary levels, not hitherto considered possible, actually occur.

The data from which Table 1 was compiled are all to be found in the tables of band analysis (Tables 2 to 47). All of these except Tables 5, 6, 7

and 8 give only principal, or "vertical" series of the different band systems, which contain in many instances numerous "horizontal" branches. These horizontal branches are all produced by combinations of the systems of Tables 5, 6 or 7 with the principal series given in the other tables.

Most of the classifications of subordinate band systems was accomplished by others. I have added a few sub-systems, and subdivided a few others, as will appear in the presentation which is to follow; but I wish the reader to recognize, as I do, that what I have to present, which is new, could not have been contributed by me if the work of others had not laid the groundwork of classification of the individual band systems which are the most outstanding.

In Table 1 each level is designated for identification by the letter *a* or the letter *b*, or by combinations of two or more letters *a* and *b* in succession. This designation is given in the first column of Table 1. It is followed in the next column by the wave number of the level, and in other columns or in vertical lines to the right of the wave numbers of the levels are given wave numbers of differences between pairs of levels. These differences are either spectral lines, in the exceptional case of the primary sub-system, or the nulls of band systems; or differences which combine with principal nulls to form subordinate nulls of the band systems; or, in some instances, the differences between nulls and the first band lines of individual bands. In some exceptional cases, it may be remarked, bands begin with a line instead of a null.

All the levels designated by the letter *a*, *aa*, *aaa*, without the letter *b*, are primary levels.

The level designated by the letter *b* is not a primary level. It is the highest frequency "secondary" level. Its quantum number is not 1, but .9651. This level is not computed by means of a series formula, as was the Rydberg number 109678, but is evaluated by the following combinations:

<i>b-aa</i>	90334.93	for which see Table 9, p. 147.
<i>b-ab</i>	98991.55	for which see Table 14, p. 153.
<i>b-aab</i>	117336.49	for which see Table 16, p. 154.

It will be noticed that the combination *b-aa* is a combination between a primary level and one which is not primary.

This level *b* will receive further discussion. We are here interested in showing how Table 1 was compiled. All the levels in this table were found by the simple processes of addition or subtraction of numbers discovered in band analysis. After they were so found, it was possible to discover series relationships between them. When such series relationships were indicated it was possible to predict the neighborhood in which other levels might be found, and by search to extend the classification system.

In Table 1 will be found a series of levels designated by letters *b* only. Their quantum numbers may be compared as follows:

Level	Wave No.	Quantum No.	Difference
<i>b</i>	117754.43	.9651 = 1 \times .9659	
<i>bb</i>	29326.52	1.9338 = 2 \times .9669	.0018
<i>bbb</i>	12988.66	2.9059 = 3 \times .9686	.0017
<i>bbbb</i>	7273.20	3.8838 = 4 \times .9708	.0022
<i>bbbbb</i>	4618.89	4.8729 = 4 \times .9756	.0038

Or we may express these relationships in the form:

$$\begin{aligned} 117754.43 &= 109678 \div (9651)^2 \\ 29326.52 &= 109678 \div 2 \times (.9651 + .0018)^2 \\ 12988.66 &= 109678 \div 3 \times (.9651 + .0035)^2 \\ 7273.20 &= 109678 \div 4 \times (.9651 + .0057)^2 \\ 4618.89 &= 109678 \div 5 \times (.9651 + .0095)^2 \end{aligned}$$

The similarity of this progression to that of the primary levels is apparent. The difference is that the quantity in parentheses is not a constant, but increases in a regular manner.

With the exception of the combination *bb-bbb*, which gives the 1-1 level of Table 3, these *b* levels do not combine with one another to give nulls of principal bands. They all enter into other combinations, as indicated in Table 1, so that their wave numbers have been determined with considerable precision, and the combinations are not doubtful.

Another series of levels in which quantum numbers increase approximately, but not exactly by 1 is the following:

Wave No.	Quantum No.	Difference
29326.52	1.9338 = 2 \times .9669	
12707.51	2.9378 = 1 + 2 \times .9689	.0020
7055.21	3.9427 = 2 + 2 \times .9713	.0034
4478.98	4.9510 = 3 + 2 \times .9755	.0042
3093.95	5.9539 = 4 + 2 \times .9770	.0015

The level *bb* combines with each of these other levels to produce principal band nulls. All of these levels also enter into other combinations by which their position in the table may be found with precision, and the table checked by internal balancing.

The schedule on opposite page provides formulas capable of accounting for each of the first fourteen levels of Table 1. The schedule may be extended to include not only all the levels listed in Table 1 but all levels that could be accounted for by any number of letters *a* and *b* in any sequence.

In order to apply these formulas it is necessary to know the value to be assigned to the variable *b* in each formula, for this value is known to vary, although in a systematic way. But if the value of *b* is known for one configuration, or formula, for example for the level designated by *abba* or *aabba*, it is possible to compute approximately what the wave number should be for some other combination which differs but slightly from the one known, such as *babba* or *abba*. This method was much used by me in the search

for clues to the interconnections of the various sub-systems which make up the many lined spectrum of hydrogen.

$$\begin{aligned}
 b \quad \nu &= \frac{N}{b^2} \\
 a \quad \nu &= \frac{N}{a^2} \\
 ba \quad \nu &= N \left[\frac{1}{b^2} - \frac{1}{a^2} + \frac{1}{(2a)^2} \right] \\
 bb \quad \nu &= N \left[\frac{1}{b^2} - \frac{1}{b^2} + \frac{1}{(2b)^2} \right] = \frac{N}{(2b)^2} \\
 aa \quad \nu &= N \left[\frac{1}{a^2} - \frac{1}{a^2} + \frac{1}{(2a)^2} \right] = \frac{N}{(2a)^2} \\
 ab \quad \nu &= N \left[\frac{1}{a^2} - \frac{1}{b^2} + \frac{1}{(2b)^2} \right] \\
 bba \quad \nu &= N \left[\frac{1}{b^2} - \frac{1}{(2b)^2} + \frac{1}{(3b)^2} - \frac{1}{a^2} + \frac{1}{(2a)^2} \right] \\
 aba \quad \nu &= N \left[\frac{1}{b^2} - \frac{1}{(2b)^2} + \frac{1}{(2b+a)^2} - \frac{1}{a^2} - \frac{1}{(2a)^2} \right] \\
 bbb \quad \nu &= N \left[\frac{1}{b^2} - \frac{1}{(2b)^2} + \frac{1}{(3b)^2} - \frac{1}{b^2} + \frac{1}{(2b)^2} \right] = \frac{N}{(3b)^2} \\
 abb \quad \nu &= N \left[\frac{1}{b^2} - \frac{1}{(2b)^2} + \frac{1}{(2b+a)^2} - \frac{1}{b^2} + \frac{1}{(2b)^2} \right] = \frac{N}{(2b+a)^2} \\
 baa \quad \nu &= N \left[\frac{1}{a^2} - \frac{1}{(2a)^2} + \frac{1}{(2a+b)^2} - \frac{1}{a^2} + \frac{1}{(2a)^2} \right] = \frac{N}{(2a+b)^2} \\
 aaa \quad \nu &= N \left[\frac{1}{a^2} - \frac{1}{(2a)^2} + \frac{1}{(3a)^2} - \frac{1}{a^2} + \frac{1}{(2a)^2} \right] = \frac{N}{(3a)^2} \\
 bab \quad \nu &= N \left[\frac{1}{a^2} - \frac{1}{(2a)^2} + \frac{1}{(2a+b)^2} - \frac{1}{b^2} + \frac{1}{(2b)^2} \right] \\
 aab \quad \nu &= N \left[\frac{1}{a^2} - \frac{1}{(2a)^2} + \frac{1}{(3a)^2} - \frac{1}{b^2} + \frac{1}{(2b)^2} \right]
 \end{aligned}$$

I did not, in fact, employ these formulas without having in mind some idea as to the origins of the radiations thus classified; but in classification I always relied upon the consistency of the numerical results, and not upon whether or not they sustained any of my preconceived opinions. Therefore I think it best to present the results of classification altogether independently of interpretation, leaving the latter to be considered after the analysis has been shown to be mathematically correct and self-consistent.

The Alpha Band System

A beginning of the classification of the wave numbers of the many lined spectrum was made by Fulcher, who picked out certain rather bright lines that are relatively intensified by low pressure during electrical excitation. He arranged these lines into groups known as the Fulcher bands. These bands were later incorporated into a much larger group or sub-system known as the alpha band system. It will facilitate our discussion of other band sub-systems to begin with the alpha band system, not because all other systems resemble it closely, for many of them do not, but because it is the most regular of all the hydrogen sub-systems except the primary, and the one about the classification of which there can be the least doubt.

The alpha system usually is treated as a single system. However, it may be treated as a combination of two systems, one of which enters into combination with other systems quite independently of the alpha system. In Table 3 (p. 141) are given the lines and nulls of the principal series of the alpha bands. The first band of this series is designated 0-0, using the usual designation employed in classification, to avoid confusion, without regard to its usual interpretation. The second band is designated 1-1, the third 2-2, and so on. Each of the first four bands has three branches, designated respectively *P*, *Q* and *R*. The *Q* branches of the first four bands contain the lines of four of Fulcher's bands. It will be noticed that there are *P*, *Q* and *R* branches for the first four bands only, though there are *Q* branches for five more bands in the series.

In Table 3 are given not only the nulls and lines, but also the "first" and "second" differences in wave numbers between neighboring lines in each series. The first wave number given for the *Q* branch of the 0-0 band is 16611.43, for which the intensity is 10. This is one of the most intense lines in this spectrum. The next line of this branch has wave number 16596.37. The difference between these is 15.06. The difference between 16596.37 and 16573.94 is 22.43. The difference between 22.43 and 15.06 is 7.37. This is called a "second difference." The second differences obtained for this *Q* branch are of the same order of magnitude, and progress in a regular manner. This is the first method available for classifying band lines. It is not always, or even generally applicable, but has rendered very valuable service. The number 16619.01 is obtained by extrapolation, and is called a null. Very often several branches have the same null, as is the case with the *P*, *Q* and *R* branches of the alpha bands. This rule, however, is not universal, it being quite common for a null to be the origin of two bands, usually designated as *P* and *R*; but there are quite a number of bands that have hitherto been classified as *P* and *R* branches with presumably a null in common, which actually have different nulls.

Before proceeding to discuss the significance of the first and second difference numbers in band classification, let us turn our attention to the other bands of the alpha system to which the bands of this principal series are related in a very interesting way, which has aided greatly in classification, though at the beginning of classification it was entirely unknown.

The whole of the alpha system as classified by Richardson is given in Table 4 (p. 143). The bands are arranged in vertical columns and in horizontal rows. The 0-0, 1-1, 2-2, 3-3 bands are placed in the same vertical column, as in Table 3, though this is not the usual arrangement, which is to place the bands numbered 0-0, 1-0, 2-0 in the same column, thus bringing like difference numbers, such as 2521.07 and 2521.08, in the same column. In my opinion, the 0-0 band is more directly related to the 1-1 band than to the 1-0 band, and the arrangement used in Table 3 is preferable on that account, as will be shown in what follows. But however the bands are arranged, it will be seen that the difference number 2521.07, or a number

differing therefrom by such small amount that the discrepancy might be ascribed to error, occurs seven times in Table 4, and other numbers of different, but similar magnitude occur frequently in the table, and in regular order.

These numbers, and other numbers which are found in band analysis separating bands in similar manner, will be called "horizontal difference numbers." The horizontal difference system associated with the alpha band system is assembled in Table 5 (p. 145), where first and second differences are given. This same system combines in a similar manner with other principal series, and a systematic search for these differences, once they were known, made it possible to classify other sub-systems which scarcely could have been classified with reasonable assurance otherwise.

There are other horizontal difference systems which combine with other principal series in a similar manner. For the sake of having the more important of these close together for ready reference, the most extensive of these horizontal systems is given in Table 6 (p. 145) and the next in importance in Table 7 (p. 146). In Table 8 (p. 146) are given differences which we will encounter in somewhat different combinations, but which have been found with reasonable accuracy as Raman differences.

We now return to consideration of the principal series as given in Table 3. The lines all were classified by Richardson, the nulls all extrapolated by myself. The principal null, 16619.01, will be found as a difference in Table 1, where it is ascribed to the combination *bb-abb*. We will have to justify these levels, but first we must justify the null. In the *Q* branch of the 0-0 band the second differences diminish regularly. In the 1-1 branch they diminish regularly from 7.31 to 6.72, and then comes 7.57 which is practically identical with the first difference in the 0-0 band, and the first second difference in the *R* branch thereof. In the *Q* 2-2 branch the second differences again diminish regularly. We also observe that the same second difference numbers recur in different bands, for example, 6.97 in 0-0, 6.94 in 1-1, 6.98 in 2-2 and 6.72 in 1-1, 6.71 in 2-2, 6.71 in 3-3.

A similar recurrence of like, almost identical difference numbers, both large and small, is a common feature of the hydrogen spectrum; but the usual method of band analysis conceals the significance of these recurring differences, and even conceals many of the differences except those which are associated with "horizontal" series, given in our Tables 5, 6 and 7. Such differences occur not only as second differences from line to line, but the same numbers occur quite frequently as first differences between null and first line in both *Q* and *R* series, as will be observed in what follows. They also occur as simple differences between null and null. To discover the significant ones, which are very often recurring, we must consider the nulls of the principal series of the alpha bands in the order 0-0, 1-1, 2-2, etc., rather than in the order 0-0, 1-0, 2-0.

The second differences progress regularly in the *R* 0-0 branch, though not in the same manner as in the *Q* branch. In the *R* 1-1 branch, however,

they jump from 8.75 to 11.64 and back to 9.81. If we were guided by a hypothesis requiring second differences to be regular in all cases, we would have to reject the *R* 1-1 branch. At the outset of classification studies regularities in second differences were the only criterion. Then came observable relationships between *P*, *Q* and *R* branches of the same band. But these criteria, though very helpful, did not suffice to render classifications certain. It required the discovery of the accurate applicability of the horizontal differences of Table 5 to the alpha band system to overcome all doubt as to the correctness of Richardson's classification as given in Table 4.

There are several reasons for considering the bands of Table 3 as constituting the principal series of the larger systems given in Table 4. In the first place, this arrangement gives the longest series, the greatest number of terms and includes the most intense lines. In the second place, it gives second differences from line to line which all are of the same order of magnitude. In the third place, it gives differences from null to null which are of like order of magnitude, and which we find repeatedly in the analysis of other band systems, indicating that they are simple differences between levels if such simple differences occur. These numbers, 281.11, 270.53, etc., have been allocated suitably in Table 1. Table 1 is, in fact, compounded by discovering such recurring simple differences and allocating them properly. Certain nulls are simple differences between levels, for example, the 0-0 null of Table 3. Other nulls are compounded of two or more such simple differences, as are the various other nulls of the alpha system. To make Table 1 complete it would be necessary to classify all the lines of the secondary spectrum, ascertain all nulls correctly, and account for all the differences between nulls, all differences between nulls and first lines of all branches, and all second differences from line to line wherever the systems were compounded of horizontal and vertical series, which is not always the case. Table 1 is not complete to this extent, but it extends far enough to account for the nulls of all known band systems about the classification of which there is no serious doubt, and most of the first lines of the *R* branches.

Other Band Systems

All our other tables deal with band analysis, which includes accurate determination of nulls by simple arithmetical processes of addition and subtraction. From these tables of band analysis Table 1 was compiled. This was accomplished very slowly, something being added from one band system at one time and from an entirely different band system at another time, until a general outline was found, after which it was possible to predict some previously unknown nulls and to find the bands associated with them. Such difference numbers as 2524.34, 1318.34, 281.15 and many others occur too many times in the analysis of band systems quite different from one another in structure to admit the possibility of their not being significant additive or subtractive increments of much the same character.

as the Raman increments 4162.1 and 357 of Table 8, which are known to be such increments in Raman spectra, and also occur as increments in band structure. All of these numbers which recur in different band systems have places in Table 1.

To economize time and effort on the part of the reader the most important levels in Table 1 will be discussed in the order in which they appear in the table, not the order in which they were evaluated, reference being made to the various tables of band structure as occasion arises.

The Level $\nu = 117754.43$

The wave number of the highest frequency emitted by hydrogen is 117754.43. Approximately, this level is obtainable by direct experiment. Figure 1 of the article on the ultraviolet spectrum of hydrogen by Dieke and Hopfield in *Physical Review* (October 1927) shows the absorption spectrum of hydrogen when excited hydrogen itself is the source of light. No appreciable amount of light of wave length shorter than $\lambda 849.43$ reached the plate. This wave length corresponds to wave number 117726.

This fact might be explained in two ways. The first explanation is that, although hydrogen emits light of higher frequency, such light is all reabsorbed by the hydrogen in the tube and reemitted at lower frequencies. The second explanation is that light of higher frequency is too small in amount to affect the plate, and that the chief source of light to be absorbed is the characteristic continuous spectrum of hydrogen, which therefore must have a limit at or near the observed limit. It is well known to those who have studied x-rays that "hard" x-rays cannot be excited by electron bombardment of atoms of low atomic number. I have not yet found any recorded data giving the limiting frequencies that can be excited by bombardment of the various chemical elements, and therefore do not know just what the limit for hydrogen is, though I suspect that it is at wave number 117754.43, in which case the sudden termination of the absorption line spectrum when hydrogen is the source of light would be accounted for. If hydrogen can emit radiation of higher frequency, the observed limit must be attributed to the fact that absorption is practically complete at and beyond the observed limit, and the amount of radiation to be absorbed beyond that limit must be relatively small. In this connection it is significant that if helium is used as a light source and hydrogen as the absorbing medium, ample light beyond 117723 reaches the plate, and absorption lines due to hydrogen appear beyond that wave number. The absorption band beyond this limit observed by Hopfield is given in Table 16, p. 154.

The occurrence of hydrogen lines in the region of wave lengths about one-quarter of those in the visible region has been known for a considerable time. This region is called the Schumann region in honor of the man who first investigated it. Later, Lyman found and measured the wave lengths of a number of primary lines in this region belonging to the series which

bears his name. He also discovered several groups of lines known as the Lyman bands. Since then several observers, with better apparatus, have studied this region and published their findings.

The proposed classifications of the different investigators do not agree completely, the discrepancies being greater than can be ascribed to probable inaccuracy in measurement. In this region there are lines that have been measured in absorption only, not in emission, and lines that have been measured in emission by one investigator, but not by others studying the same region. Comparatively few lines, if any, have been observed both in emission and in absorption, unless we disregard serious discrepancies in wave numbers. The Lyman bands are very intense when excited with a small quantity of argon with the hydrogen in the tube. They either are entirely absent, or are relatively weak, when no argon is in the tube, in which case other lines appear in the localities where the Lyman lines are found. A comparison of observed lines of these two systems is given in Table 13 (p. 153); but before discussing this table let us consider the least complex band system in this region, which was observed in absorption by Dieke and Hopfield, the lines of which are given in Table 9 (p. 147). The nulls in Table 9 were extrapolated by myself. If there is a level in the neighborhood of 117723, and it combines with another level to give the null of the system of Table 9, the other level must be in the immediate vicinity of the Balmer limit, 27419.50. There is no other level in that vicinity. It seems likely, therefore, that the combination is with this level, which is accurately known.

In extrapolating to obtain the null it is assumed that the second differences in the 0-0 band should be fairly regular, and should consist of differences which occur in our Table 1 as observed elsewhere. When such extrapolation is made it is found that the first differences, 138 and 96, as closely approximate differences which we have found elsewhere as the accuracy of the measurements would entitle us to expect. Thus the null is placed at 90335, which gives us the level 117754.50. This is in satisfactory agreement with other determinations of this level which will be discussed.

Dieke and Hopfield pointed out the fact that these absorption bands (as well as bands measured in emission) are separated by the horizontal differences of our Table 6, which have been evaluated accurately by classifications in the visible by Richardson. Assuming this to be correct, and that the 0-0 null has been found with satisfactory accuracy, the other nulls of the series may be computed as in Table 9 (p. 147). These computed nulls are used in computing first and second differences in band structure, and the results are satisfactory for the first four bands, as the differences 138, 96, 136, 97, 143, 98 and 133 are as close to differences more accurately determined elsewhere as the precision of the measurements would lead us to expect — in fact, they are somewhat closer than we would expect. But the second differences in bands 4-0, 5-0, 6-0; 7-0, 8-0, 9-0 are not satisfactory, and the number of lines found is greater than for bands 0 to 3, so that we

may suspect the presence of two sets of bands here, with somewhat different nulls, not hitherto separately evaluated.

The Lyman bands are very intimately related to this *B-A* absorption band system, though they are observed only in emission, and then are prominent only when argon is present. The Lyman bands, as measured by Dieke and Hopfield, are given in Tables 10 and 11 (p. 148), the nulls being evaluated by myself. The leading null of this series is the 3-0 null of Table 9.

Before discussing Tables 10 and 11, reference should be made to the sources of information about these bands. Though I have used Dieke and Hopfield's measurements in both Tables 10 and 11, the groups given in Table 11 were those first measured by Lyman. Later, those of Table 10 were measured by Witmer working in Lyman's laboratory, and reported in 1926. Werner, working in Bohr's laboratory, also reported the Lyman bands. With Witmer's paper * was published a print showing the Lyman bands as he observed them, with a small quantity of argon present with hydrogen in the excitation tube. This print shows two strong argon lines overlapping band 3-0 and largely obscuring it. Then follow bands 3-1, 3-2, 3-3, 3-4, 3-5, 3-6 with decreasing intensity in the order given, the 3-3 band being partially obscured by the first Lyman line of the primary spectrum. Then follows the band 3-7 with greatly increased intensity, and bands 3-8, 3-9, 3-10, 3-11 diminishing in intensity from 3-7. The appearance of the illustration strongly suggests the existence of two distinct series, one comprising bands 0 to 6 and one bands 7 to 11.

The null of the 3-1 band of Table 10 is derived from that of the 3-0 band by subtracting 4162.1. This difference number is accurately known as a Raman difference, and as such is given in Table 8 with other Raman differences. The other nulls are obtained as shown in Table 10, where it will be seen at a glance that the second differences 236.82, 207.50, 195.26, 281.11 and 248.66 are numbers which occur elsewhere, all but one of them occurring in Table 3. The difference numbers from nulls to first lines in both directions from the null also are found in Table 1, making reasonable allowance for errors in measurement.

I have rejected the hypothesis that the bands designated 3-7 to 3-11 belong to the same series as the bands 3-0 to 3-6 as not justified by the observations. These band lines are accounted for numerically in Table 11 as derived from a combination of the null $b-aa = 90334.93$ with the second Balmer line 20564.63, producing a null 69770.30 which I have designated 3-7 in Table 11, for purposes of identification only. Both of the combinations $b-aa$ and $(b-aa) - (aa-aaa)$ are, of course, taboo to the present assumptions as to the origin of these spectra. The differences 2524.34, etc., are the same as in Table 5 and the differences 6898.57 and 1587.00 will be found accounted for in Table 1.

When argon is not present in the discharge tube the Lyman bands either do not appear, or are relatively weak. The region in which they occur is

* *Phys. Rev.*, 28, 1224 (Dec., 1926).

then found to have other bands which have been measured in emission by several parties, but which have not been esteemed to be distinct from the Lyman bands hitherto. These other bands belong to a rather extensive system, many, but not all expected bands of which have been recorded. The latest and perhaps the most accurate records are those of Jeppesen; the next those of Hyman. Their fields of observation overlap and their classifications agree in the main, but not completely. As will be seen from the following schedule, the bands expected, nearest to the 0-Q null have not been reported in emission. The letter *J* indicates that the band was recorded by Jeppesen, *H* by Hyman, *D* by Dieke and *W* by Witmer.

		Horizontal Sequences. B									
		0	1	2	3	4	5	6	7	8	9
Vertical Sequences. A	0	<i>D</i>	<i>D</i>	<i>D</i>	<i>DJW</i>	<i>D</i>	<i>D</i>	<i>D</i>	<i>D</i>	<i>D</i>	<i>D</i>
	1				<i>JW</i>		<i>J</i>	<i>J</i>			
	2		<i>J</i>	<i>J</i>	<i>W</i>						
	3	<i>JH</i>	<i>JH</i>	<i>H</i>	<i>WH</i>	<i>H</i>	<i>JH</i>	<i>JH</i>	<i>H</i>		
	4	<i>JH</i>	<i>JH</i>	<i>JH</i>	<i>WJH</i>	<i>H</i>	<i>JH</i>	<i>H</i>	<i>JH</i>	<i>H</i>	
	5	<i>H</i>	<i>H</i>	<i>H</i>	<i>WJH</i>	<i>H</i>	<i>JH</i>	<i>JH</i>	<i>H</i>		
	6	<i>H</i>	<i>H</i>	<i>H</i>	<i>WH</i>	<i>H</i>	<i>H</i>	<i>H</i>	<i>H</i>	<i>H</i>	<i>H</i>
	7	<i>H</i>	<i>H</i>	<i>H</i>	<i>H</i>	<i>H</i>	<i>H</i>	<i>H</i>	<i>H</i>	<i>H</i>	
	8	<i>H</i>	<i>H</i>	<i>H</i>	<i>H</i>	<i>H</i>	<i>H</i>	<i>H</i>		<i>H</i>	<i>H</i>
	9	<i>H</i>	<i>H</i>	<i>H</i>	<i>H</i>	<i>H</i>	<i>H</i>	<i>H</i>	<i>H</i>		<i>H</i>
	10			<i>H</i>	<i>H</i>	<i>H</i>	<i>H</i>	<i>H</i>	<i>H</i>	<i>H</i>	<i>H</i>
	11				<i>H</i>	<i>H</i>	<i>H</i>	<i>H</i>		<i>H</i>	<i>H</i>
	12					<i>H</i>	<i>H</i>	<i>H</i>	<i>H</i>	<i>H</i>	

Note the absence of bands 0-0, 0-1, 0-2, 1-1, 2-0 and 2-1. Apparently the energy that might be expected to produce these bands has been diverted to the bands farther from the null. In the schedule the absorption bands of Dieke and Hopfield (Table 9) are indicated by *D*, the first Lyman group by *L*, and the second by *W*. In horizontal sequences the lines of successive bands of this system are separated from one another by the difference numbers' of Table 6 (p. 145). These differences were obtained accurately by Richardson, in the visible regions of the spectrum. Wave numbers of lines in the ultraviolet are not known with equal accuracy, and a number of bands either are missing or have not been recorded. The principal series of the *B-A* emission bands have been obtained by extrapolation, using the system of Table 6, where the bands have not been observed directly, and

is given in Table 12. As in all other band systems, the nulls have been extrapolated by myself.

The criteria that have been accepted as essential in extrapolating the nulls are as follows: (a) It is obvious that the "second differences" from null to null in Table 12 are of the same order of magnitude as the differences from null to null in Table 3. It is assumed, therefore, that these second differences should be selected from among numbers of such magnitude found in other band analysis and set forth in Table 1. (b) As the second differences from line to line in successive bands in Table 12 are of the same order of magnitude as one another and as various null to R_0 differences in several tables as well as line to line differences in Tables 10, 11, 12 and 36, it is assumed that the second differences to be extrapolated and the differences from null to R_0 and null to P_1 must be numbers taken from Table 1, of the appropriate order of magnitude. While we cannot accept as accurate results, and therefore not as positive identification of the smaller differences in the Schumann as in the visible region, we can place a great deal of confidence in the selection of the second differences from null to null — 248.66, 207.50, 236.82 and the like.

In Table 12c (p. 152) the nulls are given in vertical sequence, with first and second differences. The first difference, 4162.1, is also found as a Raman difference, where it is accurately known. While the second differences include several (but not all) of the differences found in Table 3, unlike that table some of the same differences occur several times, 248.66 due to *baa-aaa* occurring twice, 236.82 three times and 223.35 twice. This must have some special significance when we consider the sources of these bands. In this connection we merely note the repetition of significant differences, even in the same series of nulls.

While the 0-0 band in Table 12 has not been observed in emission, it has been extrapolated from bands that have been observed in emission in horizontal sequence relationship to it, and its null is in reasonable relationship to the null of the 0-1 band. No other conclusion seems to suggest itself than that the band which is so readily excited in absorption arises more directly from the null than that which is more readily excited in emission. The difference between these 0-0 nulls is 126.63, which is one of the differences in Table 1 found in other band systems.

According to Jeppesen's classification, the more intense lines of the Lyman bands belong to P branches of the bands B_3-A_6 to B_3-A_7 , and the classifications of our Table 10 must be incorrect. For convenience in comparison, Table 13 gives observed bands as classified by Jeppesen and Lyman bands as observed by Dieke and Hopfield and by Witmer, as arranged by myself. The difference between my classification and Jeppesen's arises from the latter's assumption that the two branches represented in his classification have a common null, while I classified the observed Lyman lines, which are intense when argon is present, without regard to those lines which are either absent or very weak when argon is present. This was done before

Jeppesen's work, and of course Jeppesen's measurements of wave length are much more accurate than the earlier measurements of others. On the other hand, many lines of all observers are reported as blends, and the published tables give no lines observed but not classified, while both Dieke and Witmer report lines not reported by Jeppesen or Hyman. For example, in band 3-4 Dieke gives a line 78808, very close to where Jeppesen reports a null. In view of the very incomplete recording of the unclassified lines in this region and the blank spaces in the chart where bands are expected, and for other reasons herein indicated, I am of the opinion that further discussions of classifications in this region should be held in abeyance, and when made, must afford an explanation of why the Lyman bands and not others are intensified by argon.

The *C-A* bands also have been measured partly in emission and partly in absorption, and seem to comprise two systems superimposed, instead of a single system, thus resembling the *B-A* bands. However, there are several distinguishing differences other than wave numbers. The *C-A* bands have *P*, *Q* and *R* branches for each band, while the *B-A* bands have only two branches. The "horizontal" branches of the *C-A* system are separated by the difference numbers of Table 7, while the *B-A* horizontal branches are separated by the differences of Table 6.

The absorption *C-A* bands given in Table 14 are as recorded by Dieke and Hopfield. The 0-0 null is derived from the combination *b-aba*. The principal series for emission as given in Table 15 derives from an 0-0 null, which is not the same as that of Table 14, but may be obtained therefrom by adding 120.80, which is a difference that should occur in Table 1 if our table were complete. This difference occurs again in Table 16.

The first vertical difference from null to null in Table 15 is taken as the same as in Table 12, but as the 0-0 band has not been observed in emission this may be in some error. I am unable to follow Jeppesen in his evaluation of the nulls for this system, or in assuming that the differences from null to null in vertical sequence are the same as in the *B-A* system, but the second differences obviously belong to the same group as the first differences from null to null in Table 3, and are found in Table 1. Errors in selection of these may occur owing to inaccuracy of data in this system, the observations being very far from complete and satisfactory, but there can be little doubt of the correctness of the general scheme.

Beyond the limit 117754, when helium is the light source, a hydrogen absorption band was observed by Hopfield, who reported the wave lengths given in Table 16. The wave numbers and differences in that table were calculated by the writer from the wave lengths. The writer introduced the first difference, 1907.02, which is *bb-aa* of Table 1, and was obtained after *bb* was accurately known from band analysis in the visible region, to which this presentation will come in due course. The second difference numbers, 63.18, 129.37, all occur in other band systems, where they are more accurately determined, and entered in suitable places in Table 1.

The null of this band therefore is known with greater precision than the nulls of the B - A and C - A absorption bands of Tables 9 and 10 from which the initial departures are not so certain. The level 417.94 is known with considerable precision from band analysis in the visible region and the combination $117336 = 117754 - 417.94$ confirms our level 117754 as set forth in Tables 9 and 10. The Hopfield band does not occur in emission.

This analysis of the Hopfield band is the only one yet offered accounting for the irregularities of the second differences in any adequate way, finding these differences irregular because they are due to discrete differences between levels, which occur elsewhere than in this particular system. Hopfield computed a formula for this system,

$$\nu = 109224 + 1900 \nu' + 59.52 \nu'^2$$

which irons out these irregularities; but the acceptance of this formula would require corrections in the wave length measurements far greater than the probable inaccuracy thereof. Only by recognition of the fact that these second differences are discrete and should not be averaged, can these lines be accounted for in any reasonable manner.

This band also offers a stumbling block to Professor Richardson's interpretation of the secondary spectrum. Richardson discusses this band on pages 96 and 97 of his book, but gives an "alternative interpretation" on pages 303 and 304, not seeming fully satisfied with either explanation. He does not attribute any significance to the irregularities of second differences in this band, and he does not find any principal null in the neighborhood of 117336 compatible with his theory.

The most complete treatment of the band spectra of hydrogen hitherto published is Professor Richardson's book "Molecular Hydrogen and Its Spectrum." It recognizes no such level as 117754 and no combinations between primary and secondary levels. In place of such combination as the writer's b - aa he attributes the 0-0 null of the B - A system to the difference between $A = 124569$ and $B = 34365$. (See his book, page 324.) The level 34365 of Richardson is used by him as the level of highest wave number contributing to the important band systems of our Tables 23 to 33 where the writer has selected the level $ba = 35375.27$. I do not agree with any of the assumptions by which the level 34365 is computed. It is not derived by simple addition and subtraction, as are all of the levels in Table 1. Richardson's level $A = 124569$ is determined from B by adding to 34365 the null 90204, which agrees closely enough with the null of the emission bands 90208 of our Table 12.

On page 59, in his preliminary theoretical treatment, Richardson computes that "the main strength of this spectrum should extend to about wave number 120,000." This is actually closer to the writer's level 117754 than to $A = 124569$. I hold that there are four errors involved here:

(a) The computation of $B = 34365$ by series formula on wholly unjustified premises.

- (b) The assumption that this level enters a combination to produce the $B-A$ band origin.
- (c) The denial of possibility of combinations with any primary levels in this band system.
- (d) Failure to recognize the independent evidence of the level at about 117754.

Richardson uses the level $A = 124569$ and the 0-0 null of the $C-A$ band system to find a level $C = 25475$, for which also I find no justification. The use of these three levels $A = 124569$, $B = 34365$ and $C = 25475$ by Richardson instead of $b = 117754$, $ba = 35375$, $aa = 27419.50$ and $aba = 18763$ accounts for most, but not all the discrepancies between Professor Richardson's analysis and mine. It results in the general table of levels given by Richardson (pp. 324 to 329) possessing no internal evidence of correctness due to balancing, as is manifested by our general Table 1, which is not based upon any *a priori* assumptions, but which perhaps may afford us *a posteriori* reasons for revising hypothesis.

We shall now continue our discussion showing that the levels given in Table 1 and their differences, are capable of accounting for all the nulls of the various known bands for which the principal series are given in the tables of band structure, Tables 2 to 45, leaving justification for the combinations on physical grounds entirely out of the argument until the mathematical soundness of the analysis has been made clear.

The Level $bb = 29326.52$

The next level to be considered is designated bb in Table 1 and its wave number as there given is 29326.52. There are several reasons for considering this before the level ba , the chief of which are as follows:

(a) This order will explain the allocation of several difference numbers which will be of use to us in determining accurately the level 35375.27.

(b) I am in perfect accord with Richardson as to many of the combinations entered into by the level 29326.52 and my evaluation of the level is very nearly the same as his, so that in treating certain band sub-systems there is no controversy involved as to the level 29326.52.

(c) We have already discussed in a preliminary way the alpha bands for which the 0-0 null is derived from a simple combination with the level 29326.52. These bands are given in Tables 3 and 4.

The principal series of a band system very similar to that of Table 3 is given in Table 17 (p. 155). This combines with the same "horizontal" difference system as Table 3, the horizontal system being given in Table 5. This system was classified by Richardson, with the exception of a very few lines added by myself, which are indicated by the letter v . Some of the series have been extended somewhat by others, subsequent to Richardson's publication, but these extensions are not included in Table 14, though not at all discordant.

An outstanding similarity between the structure of the systems in Tables

3 and 17 is that of the second differences between nulls. In fact, the difference numbers 281.01, 270.49 and 259.84 occur in both tables.

The principal series of another band system which also has branches separated from it by the differences of Table 4 is given in Table 18 (p. 156). In this case, however, there are no differences between nulls equal to any of those in Tables 3 or 14. However, the same differences as occur in Table 18 are found again in a band system in the infrared region, given in Table 43 (p. 170).

Besides the systems outlined in Tables 3, 17 and 18 which have P , Q and R branches for some of the bands, but not all, Professor Richardson found a band given in Table 19 (p. 156), for which only a Q branch is known.

It was known from the work of Curtis that certain bands in helium have their nulls related in a manner that can be expressed approximately by a Rydberg-Ritz formula. Richardson found the 0-0 bands of our Tables 3, 17, 18 and 19 related in a similar manner. His formula as given on page 184 of his book is:

$$\nu_0(\text{null}) = 29343.0 - N \div \left[n - .058077 - \frac{.044991}{n^2} \right]^2$$

The number 29343 corresponds to my level 29326.52, which is believed more accurate, as it has been found by simple addition and subtraction, without resort to series formula.

Assuming, however, that there is a level in the neighborhood of 29326.52, the difference between it and the Balmer limit, aa , is in the neighborhood of $29326.52 - 27419.50 = 1907.02$, which obviously is very close to Hopfield's difference 1900, and in our Table 16, we have used the figure 1907.02 as correct. By analogy it might be supposed that there were levels that would differ from the primary levels 12186.44 and 6854.87 in a similar manner, and that the differences might be found among the differences from null to null in Table 3. Such was found to be the case, and the writer, after a very long period of study which involved careful consideration of all the known band systems, succeeded in allocating all the difference numbers such as 281.11 in Tables 3, 17, 18 and other tables not yet discussed, into suitable places, as differences between levels in Table 1, mostly on Sheet 2. The completion of this task so as to avoid all discrepancies was a matter requiring several years, although verification of the self-consistency of the table now is a relatively simple matter. The numbers which directly link primary levels to secondary levels in this way are,

$$248.66 = 12435.10 - 12186.44 \quad \text{and} \quad 236.82 = 7091.69 - 6854.87$$

or

$$248.66 = baa - aaa \quad \text{and} \quad 236.82 = baaa - aaaa$$

It then seemed possible that band nulls might arise by such combinations as $bb-baa$, $bb-aaa$, $bb-baaa$. As the level bb was known approximately by a series formula, the positions of those nulls could be found approximately by simple subtraction. The bands outlined in Tables 20, 21 and 22 (p. 157),

were found in this manner. They are of a type of structure quite dissimilar from that of the bands in Tables 3, 17 and 18, which structure will be discussed in connection with the levels *baa* and *baaa*; but it was found that by taking an initial null to R_0 difference 59.56 between null and first line in Table 20, and other differences which occur elsewhere in Table 1 as differences from line to line, the successive bands in Tables 20, 21 and 22 are separated by the same difference numbers as occur between nulls in Tables 3 and 17.

The level $aaa = 12186.44$ is a well known primary level. The difference 248.66 is accurately known not only from the bands of Table 3 but from other band systems not yet discussed. By adding the nulls to these levels we get an accurate value of $bb = 29326.52$, which is adopted in Table 1.

As set forth in Table 1, this level "combines" with at least twelve other levels to give rise to 0-0 band nulls, and through them to band systems which have been classified. Knowing this level and the respective nulls the other levels can all be found. This gives us directly the levels *abb*, *baa*, *aaa*, *abba*, *aabba*, *aabbaa* and others, though further confirmation of each combination should not be overlooked.

The Level $ba = 35375.27$

As indicated in Table 1, *ba* is the level of highest frequency which combines directly with at least four other levels to give the principal nulls of band systems in the visible or near ultraviolet regions. Of these the combination *ba-bbaa* produces a null 21621.84 from which many subordinate band systems are derived; all of those so derived that have been classified have branches separated in horizontal sequences by the numbers given in our Table 6.

The horizontal differences in Table 6 occur more frequently than any other horizontal differences found by spectrum analysis. The determination of the combination producing the initial difference 1318.34 is of great importance in our scheme. This is ascribed to *baa-bbaa* = - 1318.34, as entered in the table, which gives $bbaa = 13753.44$. It was guessed that *ba* combines with *bbaa* giving the null 21621.84, and that another band system originated in the combination *ba-aaa*. The principal series of these two systems are given in Tables 23 and 24 (pp. 158 and 159).

The lines of the principal series of both of these tables are known to be correct beyond reasonable doubt by the horizontal difference system of Table 6 (p. 145). The classification of the band lines is entirely due to Richardson and his coworkers. The nulls were difficult to ascertain exactly because the second differences in vertical sequences are not regular, as in the bands of Table 3, as may be seen on inspection of the respective tables. Therefore, it was only after most of the difference numbers 301.51, 291.23, 36.87, 26.58, etc., had been allocated properly in Table 1 that the initial difference numbers 20.21 in Table 23 and 26.58 in Table 24 could be selected. By selecting 26.58 as the initial difference in Table 24 the null is determined

as 23188.83. Adding this to the Paschen level gives us $ba = 35375.27$, which is accepted as correct. There is no discrepancy between the level found in this way and that found by adding the null of Table 23 to the level 13753.44. The level 35375.27, however, is fully confirmed by two other combinations producing nulls as given in Tables 34 and 35 (p. 164) which will be discussed in connection with levels aba and abb . The bands of Tables 25 and 26 (pp. 159 and 160) are derived from the null of Table 24, and the bands of Tables 27 to 33 (pp. 160–163) are derived from the null of Table 23.

The Levels bba and aba

I have not found any direct combination of bba with either b , ba or bb . It does not follow necessarily that there are no such combinations, because bands in the Schumann region have not been classified fully. There is, however, a band system which has been rather fully investigated by Professor Dieke that appears to have bba for a contributing level. The principal series of this system is given in Table 36, the 0-0 null being at about 12709.43.

In horizontal sequences, the bands of Table 36 (p. 165) combine with the differences of Table 7, which bear a remarkable resemblance to those of Table 5, but begin with a different number, 2308.82 instead of 2524.34. The progressions also are less regular, as indicated in Table 7, the numbers 2274.57 and 2257.67 sometimes occurring where 2277.43 and 2261.98 would be expected, were the progressions regular, and similar irregularities occurring elsewhere. But I do not doubt the correctness of Professor Dieke's analysis in spite of this peculiarity.

Derived from the null 12709.43 are several other groups, or sub-systems, the principal nulls of which are given in Tables 37–40 (pp. 166–168). The differences separating these nulls, 281.11, 248.66, 311.63, 236.32, are identical with differences from null to null in Table 3.

The principal null 12709.43 is ascribed to the combination $bba-bab$, neither of which has yet been found independently; bba , however, may also be found by adding the difference number 311.63 to the level aba which our table gives as 18762.88, a level known from the combination $ba-aba = 16612.39$, the principal null of the band system outlined in Table 34.

This system (Table 34) like those of Tables 20, 21 and 22 has a structure quite different from that of those bands where lines of horizontal branches are separated by the difference numbers of Tables 5, 6 or 7. The compounding is more direct; but our familiar number 59.56 is taken as the first departure from the principal null; and we find successive nulls separated by the well known differences 248.66 and 236.82.

The Levels bbb, abb, baa, aaa: 12988.26, 12707.51, 12435.10, 12186.44

The level abb is obtained by subtracting the 0-0 null of Table 3 from the level bb . The level bbb may be obtained by adding the frequently recurring difference 281.11 to abb or by subtracting the 1-1 null of Table 3 from the

level bb . The level baa may be obtained by adding 248.66 to the aaa level 12186.44, or by subtracting the null of Table 20 from the level bb .

The level abb , however, also combines with ba , giving the null 22667.76 of Table 35. This band was found by Richardson, who instead of considering it an 0-0 band classified it as a 1-0 band in his Table 67 on his page 189, the 0-0 band of which this writer rejects as having no relation to this band. Most of the bands with nulls derivable from ba as one level combine with the differences of Table 6 to produce horizontal branches. This one combines with the differences of Table 5, not Table 6.

The Levels $bab = 6365.08$ and $aab = 6157.58$

The combination $bba-bab = 12709.43$, producing the principal null of Table 36, has already been referred to in discussing the level bba . No combination of bab with bb or ba has been found; and any combination of bab with a level of smaller wave number would be so far in the infrared region that it has not been observable. But there are combinations of this level which produce wave number differences between bands of the same system.

The difference $bab-aab = 207.50$ is found in the band systems of Tables 10, 12, and probably between the 6-6 and 7-7 nulls of Table 3, although sufficient lines to find the 7-7 null accurately are not recorded in that table.

Other differences involving bab and aab and other levels, which are otherwise known, are as follows:

Table 23 $baaa-bab = 726.61$	$baab-aab = 934.11$
24	$pbbb-aab = 855.78$
	$baab-aab = 900.41$
26	$aaaa-aab = 679.29$
28 $bbbb-bab = 908.12$	$baab-aab = 900.41$
42	$bbba-aab = 1168.12$

The Level $bbaa = 13753.44$

This very important level has already been discussed in connection with ba , with which it combines to produce the principal null of the most extensive band system of the hydrogen spectrum. It is accurately known by that combination and also by the combination $baa-bbaa = - 1318.34$, the leading difference of Table 6.

This level, however, also combines with others to give the three important differences 36.87, 301.57 and 328.09, as well as to produce the principal nulls of Tables 41, 42 and 43 (pp. 168, 169, and 170).

The classification of the bands in Tables 41 and 42 was begun by Richardson, but the work was revised and extended by Dieke, from whose publication the wave numbers in these tables and their arrangement, were taken. I have, however, split up this band system as given by others into

two, giving the principal series of one of these in Table 41 and of the other in Table 42.

The combination $bbaa-aabb$ in Table 41 gives us a second direct confirmation of the level $417.94 = aabb$ which in combination with $b = 117753$ gives the null of the Hopfield band (Table 16). The differences 521.07 and 764.78 are accurately accounted for in Table 1.

The combination $bbaa-bbb = 6480.24$ gives a principal null in the infrared region beyond the observable band branches, and involves extrapolation from the observed and published lines. The lines given in Table 42 are extrapolated by the use of the difference numbers of Table 6, which apply to the observed bands of this system. The use of the difference 1168.12 to extrapolate the 0-0 null is justified by the accuracy of the results.

The band system of which the principal series is given in Table 43 is another of those which has been troublesome to place in general classification schemes because the leading series lie so far in the infrared as to have escaped observation. The lines in Table 43 have been obtained by horizontal extrapolation from the lines recorded and classified by Richardson, using the difference system of Table 5. What Richardson assumed to be the 0-0 band is here taken to be the 1-0 band.

The justification for this is that otherwise the differences from null to null in the 0-0, 1-1, 2-2 sequences cannot be accounted for. With this arrangement, however, several of these differences are the same as the differences in the visible band system of Table 18. Furthermore, the initial differences from null to R_0 lines, 52.31, 49.61, etc. with this arrangement are the same as differences found elsewhere in other band systems, and as given in Table 1.

This band system of Table 43 differs from the systems of Tables 3, 17 and 18 which have horizontal branches governed by the system of Table 5 in that it has no Q branches, the P branch possessing a P_1 line which is absent in the others referred to. This fact may be important in interpretation, but of itself throws no light on classification.

The bands of Tables 44 and 45 offered considerable difficulty. The horizontal sequences are those of Table 6, but prior to 1942 I could not discover any combinations connecting these bands with the level ba , with which that horizontal system usually is associated. I therefore ascribed these bands to combinations with the level bb , which I now think erroneous. The connections with ba indicated in the tables are more suitable.

In Table 46 is given the 0-0 band of another group of bands which are separated by the horizontal differences of Table 6, but having bb , not ba , for the level of highest frequency, which is unusual. Professor Richardson gives this group in his Table 28. I ascribe the origin to $bb-baaaa$.

In Table 47 (p. 172) I give the 0-0 branch of a group which Richardson designates as the 4142.8 progression. I have ascribed the origin to $bb-bbaaa$. In this case it is not possible to ascertain the null with accuracy by extrapolation, because no lines are recorded sufficiently near the null.

The horizontal difference numbers which head Tables 5, 6 and 7 and the largest Raman difference in Table 8 are all accounted for in Table 1. I had difficulty in allocating the numbers 2524.34 and 2308.82 chiefly because no band is found resulting from a combination of either *bb* or *ba* with *bbbbaa* or *abbaaa*.

Probably when Sheet 3 of Table 1 has been corrected and extended to include all levels assignable to line molecules designated by five letters *a* and *b* the differences 2524.34, 2308.82 and 4162.8 may have to be assigned to other combinations than those indicated in Table 1, Sheet 1. Those assignments must be regarded as provisional.

In my opinion, the repetition of the same difference numbers in various tables of band analysis and the complete balancing of Table 1 for all level differences involving levels represented by not more than four letters *a* and *b* is convincing evidence that the same causes or combinations operate in different band systems, and that the primary system and the various secondary sub-systems are related, the secondary systems requiring primary levels for their development, mathematically considered, quite apart from any interpretation that may be placed upon the significance, or origin, of the levels themselves.

The number of simple differences between levels revealed by band analysis is large. Most of these differences are small, and should be allocated to levels which in this system of nomenclature are represented by five or more letters *a* and *b* in line. It has not been possible to allocate many of these small differences with precision, or to extend Table 1 to include all the levels represented by a symbol of five letters. The chief reason for this, I think, is the lack of precision of wave numbers of the lines in the Schumann region. If wave numbers of lines in that region were known as accurately as those in the visible region it would be possible to allocate many differences which are not now known with sufficient accuracy.

The certainly known combinations between primary levels and levels which are not primary are:

<i>b-aa</i> = 90334.93	<i>bb-aaa</i> = 17140.08	<i>baaa-aaaa</i> = 236.82
	<i>ba-aaa</i> = 23188.83	
	<i>abb-aaa</i> = 521.07	
	<i>baa-aaa</i> = 248.66	
	<i>bbaa-aaa</i> = 1587.00	
	<i>baaa-aaa</i> = 5094.75	

The repetition of the same difference numbers between nulls in vertical sequence, as shown in the various tables of band analysis, is one of the most striking features of the band spectra, when the bands are arranged in the order used in the tables. The differences which are most commonly repeated are:

<i>baaa-aaaa</i>	= 236.82	Tables 3, 12, 17, 32, 33, 36
<i>baa-aaa</i>	= 248.66	" 3, 12, 18, 32, 36
<i>bbb-abb</i>	= 281.15	" 3, 12, 14, 26, 32
<i>bba-aba</i>	= 311.68	" 12, 14, 33, 42
<i>bbbb-abbb</i>	= 259.64	" 3, 12, 14, 19
<i>aaaa-aab</i>	= 900.41	" 21, 24, 25, 29
<i>bbaa-bbb</i>	= 764.78	" 27, 28, 38
<i>bbb-aaa</i>	= 521.07	" 20, 27, 38
<i>baab-aaab</i>	= 223.33	" 3, 12, 32

Many of the numbers evaluated by analysis of the hydrogen spectrum as differences between pairs of levels are found by suitable analysis of spectra of other elements. This will be shown in Chapters 4, 5 and 6. It suggests the hypothesis that atoms of larger atomic number than 1 are complex and that some of them contain hydrogen, which may be separated by excitation and contribute to the development of spectra of other chemical elements.

In keeping with this hypothesis, in the chapters to follow I will regard each "level" for which the wave number is evaluated in Table 1 as due to a special molecule of very definite configuration in which hydrogen ions and electrons equal in number are arranged in lines, there being two axes in which an ion may be aligned; designated by the letters *a* and *b*. The notation by which the levels are designated in Table 1 may then be regarded as indicating the configurations of the molecules responsible in some manner to be ascertained for the wave numbers of the levels.

These configurations are most conveniently regarded as static, all the particles being poised with respect to one another. For the purpose of assisting analysis, this conception is sufficient. If, however, it is to become part of a theory and not merely a hypothesis it must be shown to be consistent with known theoretical principles of mechanics and electromagnetics. This will be undertaken in the second part of this book, after spectra of various elements have been compared for the express purpose of revealing probable community of origin, in Chapters 3 to 7.

Chapter 3

The Spectrum of Deuterium

The spectrum of deuterium is analogous to that of hydrogen, and its lines may be classified in a manner patterned after the classification of hydrogen lines, at least for those portions of the deuterium spectrum that have as yet been grouped into band series. The primary lines of deuterium differ so slightly in wave number from those of hydrogen that their classification is easy. The secondary lines, however, offer greater difficulties, because the atomic limits, or levels, differ more than in hydrogen. The limit of the primary spectrum of deuterium is about 109708 — 30 wave numbers greater than that of hydrogen, 109678. The limit of the secondary spectrum of deuterium is about wave number 118118 — 364 wave numbers greater than the corresponding limit for hydrogen, 117754.43.

A comprehensive investigation of the spectra of deuterium, hydrogen and mixtures of deuterium and hydrogen in various proportions was in progress at Johns Hopkins University before the war, but it has not been completed, nor have all the data been published; hence it is not yet possible to prepare a table for deuterium similar to that of Table 1 for hydrogen in Chapter 2. The band lines of deuterium which have been published correspond to those of hydrogen summarized in Tables 4, 12, 15, 30, 42 and 43. The "horizontal" differences have been evaluated for pure deuterium corresponding to those for hydrogen given in Tables 5, 6 and 7. There are thirty more principal "vertical" series classified for hydrogen than are yet classified for pure deuterium, not including the absorption spectra in the Schumann region, for which nothing has been published for deuterium at this writing.

For comparison I give in Table 48 the lines of the *R* branch of the initial band of Tables 3 and 4 of Chapter 2, with first and second differences, and the corresponding lines and differences of deuterium, and also the differences between corresponding lines of the two elements. This is the most regular band of both elements. It will be observed upon inspection that the first and second differences from line to line are greater in hydrogen than in deuterium, and that the differences between corresponding lines are by no means proportional to their wave numbers, as they are when the primary lines are compared in the same manner. Thus, although the two spectra are similar in structure, the differences evaluated by band analysis must be determined independently.

The progressions in wave numbers of the principal series of the alpha bands are given for comparison in Table 48 (p. 172), and the horizontal com-

bining difference numbers. In Table 49 corresponding levels of hydrogen and deuterium are compared, in so far as they have been evaluated for deuterium, the differences being given in the middle column. It is evident that some of these differences are positive and some negative. This would be difficult to account for if the only difference between the hydrogen atom and the deuterium atom were in mass concentrated at the center of the atoms, for then we might expect all levels to be affected in like manner. It is clear from comparisons of the many lined spectra that mere differences in mass of the component atoms could not produce such outstanding differences as these in keeping with any theory of structure yet known. These differences, however, must be capable of interpretation in a manner which will throw light upon the true structure, whatever that may be.

It is definitely known from observations other than spectroscopic that in mixtures of hydrogen and deuterium there are molecules of mass numbers 2, 3 and 4. The molecule of mass number 3 is due to a combination of one atom of hydrogen with one atom of deuterium, and is designated by HD.

At Johns Hopkins University Professor Dieke and others have observed the spectra of mixtures of hydrogen and deuterium in various proportions and have found a multitude of lines which are not emitted by either hydrogen or deuterium alone. These require explanation, and the interpretation given them by wave mechanics is that they are emitted by the molecule HD. According to the hypothesis suggested to account for these lines, there should be present in these mixtures primary lines of hydrogen and primary lines of deuterium ascribed to solitary atoms and three band systems, one due to H_2 , one to D_2 and one to HD, but no primary lines attributable to HD. This last mentioned expectation is capable of test, with the data now available, but the existence of but one system attributable to HD cannot be tested until most of the very numerous lines not classifiable as due to either hydrogen or to deuterium alone have been classified.

The expectations of the scheme which I have used in classification of the various subordinate band systems of hydrogen into one comprehensive system in Chapter 2 are very different from those of wave mechanics. I assign two possible configurations to each variety of atom, hydrogen and deuterium. If only one kind of such atoms are present in a line molecule there are four possible forms of such molecules with two atoms in line, eight with three atoms in line, and in general 2^n possible configurations with n atoms in line. But if two different kinds of atoms are present, each with two possible configurations, the total number of varieties mathematically possible for a molecule of n atoms in line is 4^n . Therefore the number of lines of all configurations mathematically possible is vastly greater in mixtures than in either pure element alone.

If in a mixture hydrogen atoms are several times as numerous as deuterium atoms we should expect line molecules containing more hydrogen atoms than deuterium atoms to be more plentiful than those which contain more deuterium than hydrogen; the reverse would be true if deuterium atoms

were several times as numerous as hydrogen atoms. However, since deuterium atoms are about twice as massive as hydrogen atoms, and since under the conditions of excitation ions are present, there would be more rapid acceleration of the hydrogen ions than the deuterium ions in the electric field which causes the excitation. Free electrons combine with these ions, forming line molecules in excited states, which give rise to the observed spectral lines. Thus there must be segregation of the line molecules of different structures, the extent of which depends upon many factors; among these must be the gas pressure, the length of the excitation tube, the total voltage used for excitation, whether the current is continuous, alternating or interrupted, and the frequency if alternating or interrupted.

Whatever its cause or extent, segregation, or classification of the line molecules, though partial, certainly would affect the probability of formation of some types of line molecules in preference to others, and the proximity of different forms which could cooperate in giving rise to certain spectral lines. We should therefore not expect all forms of molecules composed of H and D to be equally likely. Those which are on the whole most likely would produce the most intense lines, and it probably is to those that the bands now ascribed to HD are to be attributed; but until most of the lines which occur in mixtures in different proportions have been classified the configurations to which they must be assigned cannot be determined with assurance.

We now direct attention to those lines which can be predicted as possible in mixtures by computations based upon the primary spectra of both hydrogen and deuterium. Primary lines of the both elements occur also when the secondary spectra are excited. I have designated the configuration of the atom which occurs in line molecules that give rise to the primary spectrum of hydrogen by the letter *a* and now designate the corresponding configuration of the deuterium atom by *c*. Those line molecules which contain atoms in the *a* and *c* configurations would give rise only to "levels" that must account for possible lines, if the scheme which I have applied to hydrogen also is applicable to mixtures of hydrogen and deuterium. There are four mathematically possible configurations of only two such atoms, and eight of only three atoms. The possible lines are therefore 32 in number, corresponding to the first Balmer line of hydrogen. One of these is the Balmer line of pure deuterium. The other lines are calculable by application of simple formulas based upon the simple Rydberg formula.

Professor Dieke kindly furnished me with the most accurate estimate of the wave number of the first Balmer line of hydrogen and that of deuterium, from which I computed the thirty other lines that were to be considered possible. Professor Dieke then found most of these calculated lines recorded as observed in mixtures of hydrogen and deuterium, but as yet not otherwise classified. These lines were published in 1942 in my book on the hydrogen spectrum, but I reproduce the list in Table 50 (p. 174). Professor Dieke also informed me that these lines do not occur upon excitation of mixtures

gen and deuterium in equal proportions by volume, when the conditions are such that the secondary lines do not appear. The conditions in which secondary lines are not perceptible include very low gas pressure, long-continued excitation, and the presence of positive ions. These are precisely those under which maximum segregation would be likely.

Professor Dieke also found some lines at the wave numbers for which I calculated "levels" in Table 3. The occurrence of lines where nulls have been expected in band spectra is not unusual in the helium spectra, instances being mentioned in the chapter on helium. Such facts must have great bearing upon the interpretation of the origins of spectra when they have been completely correlated. When lines are found where nulls have not been expected, they usually are diffuse, and in some cases I find that one investigator has reported a line where another has reported a null. This occurs also in hydrogen, though not so commonly as in deuterium.

Completion of the analysis of the deuterium spectrum and of the classification of all lines which occur in various mixtures of hydrogen and deuterium is in my opinion one of the most important steps awaiting accomplishment in spectroscopic science. It is greatly to be hoped that this work will begin soon, now that the war is over, be carried as far as the available time, and that all the recorded lines and the conditions under which they were emitted will be published, whether the lines are classified or not. Table 51 are calculated wave numbers of lines that should be looked for in mixtures of hydrogen and deuterium.

Chapter 4

The Spectrum of Helium

In this chapter I will show that hydrogen contributes to the development of the helium spectrum and must be regarded as an ingredient of helium. For convenience, the tables dealing with classification and analysis are arranged in order at the end of the book (pp. 175 to 181).

There are five systems of lines, the levels of which have been computed with the aid of series formulas independently of one another. The most regular of these resembles the primary system of hydrogen, corresponding lines having a little more than four times the frequencies of hydrogen primary lines. From two series of lines known as the Pickering series and the "4686" series, more than a quarter of a century ago Fowler computed for this spectrum the formula

$$\nu = 2^2 \times 109723.22 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

which gives the wave numbers of the lines to a first approximation. This formula requires some correction in view of later measurements, especially those in the Schumann region, such as given in Table 58. But, assuming it to be correct enough for preliminary purposes, the successive levels computed in accordance with it are given in the column headed He^+ in Table 52 (p. 175). This is a second order spectrum, quantum numbers of successive levels differing from one another by increments of 0.5.

Of the four other groups of lines which have been classified independently of one another, two are called "line spectra" and are usually assumed to be emitted by neutral atoms; and two are called "band spectra." Band spectra are supposed to be emitted by molecules. The lines of the two line spectra have been known since the work of Runge and Paschen in 1896. Their classification is given in Fowler's compendium published in 1922. The series are long. For my present purpose it will suffice to consider the first four levels of each series. The wave numbers of these in Table 53 are taken from Bacher and Goudsmit's "Atomic Energy States," published in 1932, which doubtless is available to all students of spectroscopy who desire to verify original sources of information of this kind. Unless specifically stated otherwise, wave numbers of levels used in the discussion in this book are from that source, although in many cases I have consulted original sources. In this case I have used also for identification purposes the nomenclature employed by Bacher and Goudsmit rather than the original designations of the levels given by Fowler.

The first two terms of the $3P^0$ series of levels are triplets of small separation, only the more intense of which is represented in the table. All the levels in Table 53 were calculated with the aid of series formulas derived from the series of lines of the "normal" series. There also are other series of lines given by Fowler as "combination" series, the levels of which do not agree well with the levels calculated from the normal series. In the present discussion these additional lines are disregarded; but in any complete treatment of the spectrum of helium they should be accounted for with precision, and the discrepancies, which in my opinion are real and not due merely to errors of measurement, must be explained.

The levels of Table 53 are of first order spectra, the quantum numbers of successive levels of each series differing by increments which approximate 1. These quantum numbers have been computed by myself, on the basis of the quantum number of the Rydberg number being 1, the Rydberg number for all first order spectra being taken as the same as for hydrogen, and not a different number for each element. Thus comparison of quantum numbers may be made on an equal basis.

Series formulas for the levels of the "doublet" system were obtained independently of series formulas for the "singlet" system, as there are no "combinations" between the levels of the two systems given in Table 53, and such interconnections of the two systems as have since been found in the Schumann region are not known with sufficient accuracy to correlate the two systems with precision. It is therefore obvious that all the levels of either system may be shifted a slight amount by either increasing or decreasing them a like amount without in any way modifying the classification of the lines. If the series formulas adopted introduce any errors, one system may require a slight shift to place it on the same basis as the hydrogen system, and the other system may require a slight shift, but of different amount and perhaps in a different direction. However, since the series of lines observed are quite long in both of these systems, the displacement of either system cannot be large and probably would not change any of the wave numbers in the table to the left of the decimal points. This is mentioned because it is not to be expected that comparisons of the spectrum of one element or of one independently classified group of lines with another independently classified group can be made without allowing for such discrepancies and correcting them if possible after critical comparisons have been made.

In the discussions to follow in this chapter I will regard the wave numbers given in Table 53 as sufficiently correct to require no correction for preliminary purposes.

The evaluation of levels in band spectra is more likely to be in error than in line spectra for many reasons. Among these may be mentioned that in most cases nulls have to be found by a process of extrapolation, and it is not always possible to select the correct initial difference between a null and the first line of a series. Principal series in band structure often are short,

and even if the nulls or band heads, which sometimes are lines instead of nulls, are accurately known, the shortness of the series makes the calculation of a suitable series formula subject to guesswork as to minor constants. In the case of the helium band systems there is the further difficulty that some important bands have their origins so far in the infrared that they have not been observed, and it is impossible to correlate one series of lines directly with another, so that, even in the same system, different series of levels are not reduced to a common reference level.

The levels of the two band systems (principal series only), according to Curtis, are given in Table 54, Part 1 giving those of the first band system and Part 2 those of the second band system, which were classified independently of one another. Curtis' levels are on the left-hand side in the tables, and levels as corrected by myself, as a result of analysis of these systems in comparison with the line systems of Table 53 and other data to be referred to, are given on the right-hand side.

Comparisons of the five independently classified systems — one a second order spectrum and the four others first order systems, according to the usual classification — reveal some outstanding similarities and differences, which may be summarized as follows:

(a) Both of the D series of Table 53 are of wave numbers slightly greater than consecutive levels of the primary spectrum of hydrogen and of alternate levels of the regular spectrum of helium, beginning with wave numbers 12186.44 and 12191.47 of Table 52.

(b) The wave numbers of the $1P^0$ series are slightly less than alternate levels of the regular spectrum of helium in Table 1.

(c) The wave numbers of the $3P^0$ series are slightly less than those of the P series of Curtis' first band system.

(d) The quantum numbers of Curtis' band P levels progress by increments of very nearly 1, with less variation than in the corresponding levels of the line system and considerably less variation than the S levels of either line or band systems.

(e) The quantum numbers of the P levels of Curtis' bands show a unique numerical relationship, thus:

$$1.928 = 4 \times .482$$

$$1.964 = 2 \times (.5 + .482)$$

(f) The quantum numbers of the S levels of the line systems show a similar unique relationship, thus:

$$1.6888 = 4 \times .4222$$

$$1.8504 = 2 \times (.5 + .4252)$$

It will simplify discussion of the levels given in Tables 52, 53 and 54 to make use of a physical or pseudophysical model of an atom, which, in co-operation with the model of a hydrogen atom, could account formally for the levels obtained by the use of series formulas. Let us assume for this purpose that each helium atom is a compound, containing two atoms of

hydrogen and one atom of another element, which I will call sub-element 2. This assumption will be found justified by the analysis to follow, even if the structure of the assumed atoms is unknown and the mechanism of emission of lines left for future inquiry. We will assign to the sub-element 2 mass number 2 and consider it as consisting of a "nucleus" which, if unaccompanied by negative electrons, would manifest to charges at a distance a charge of $+2e$. If accompanied by one electron, poised with respect to the nucleus, it would still manifest to distant charges a charge of $+e$. Although a positive ion, this particle would be in several respects similar to the hydrogen atom we used as a formal model in Chapter 2, and will be discussed in greater detail in future chapters dealing with the mechanism.

In providing a preliminary model for our hydrogen atom for the purpose of accounting formally for the respective levels assigned to different line molecular configurations in Chapter 2, it was necessary to ascribe to the hydrogen atom two configurations, designated respectively by the letters a and b . In the case of sub 2 it is necessary to admit three possible configurations which I designate a_2 , b_2 and c_2 , distinguishing them from hydrogen by the subscript 2. Two or more such atoms could conceivably combine with one another in linear configurations, and hydrogen atoms could attach themselves to the ends of the line molecules so found. Whether or not this is a physical possibility, and what limitations are placed upon the number and arrangement of such line molecules are matters for future consideration. It is not assumed on *a priori* grounds that all configurations that may be indicated by a mathematical or schematic possibility are actual. Many schematic aggregations may be impossible because the forces between adjacent particles in such lines would not render some schematic configurations coherent. Such as are both coherent and likely may be indicated to us by analysis of the levels actually evaluated by the use of series formulas, the levels accounting for the lines actually observed and classified.

The scheme is directly applicable to accounting for the D levels of the line spectra of Table 53. In the column headed H of that table are the levels of the primary spectrum of hydrogen. In the column headed He^+ are levels of the regular spectrum of helium. In other columns are wave numbers of levels that can be attributed to molecules composed of sub-atoms 2 and 1 both in the a configuration. In the column headed a_2a_2 will be found the $3D$ levels and in the column headed a_4a_2 , the $1D$ levels of the helium line spectra. These wave numbers are a little greater than corresponding levels of the regular spectra of both hydrogen and helium. Schematic representation does not require them to be so, but any adequate physical interpretation will have to explain why these levels are not intermediate between the corresponding levels of hydrogen and helium.

We now are ready to attempt to explain schematically the $1P^0$ levels of Fowler's singlet system. I find them to be accounted for as deductions from the levels in the columns headed a_2a_2 of Table 1 of differences due to

hydrogen alone, which should all occur in Table 1 if that table were sufficiently complete. If this is tenable, it should be possible to find the level $a2a_2$ by adding the proper hydrogen difference to the initial level of Fowler. The most suitable difference to select is found to be 281.15 due to bbb - abb . The first four of Fowler's singlet levels are then accounted for as deductions of wave numbers from the series in Table 52 as follows:

<i>Series</i>	<i>Difference</i>	<i>Series</i>
$a2a_1$		mP
27456.97	281.15	27175.82
12209.19	107.71	12101.38
6866.19	48.14	6818.05
4393.52	25.27	4368.25

The difference 107.71 probably is due to $abbaa$ - $aabaa$, which is not entered in Table 1 because it was not evaluated from classification of hydrogen lines, although approximately calculable, by formulae in keeping with the analysis of Chapter 2.

There is a similar parallelism between the $3P^0$ levels of the doublet line system and the P levels of Curtis' first band system. In making the comparison I shall assume that Fowler's levels are correct, and that if any shift is necessary, it must apply to the $1P$ level of the band system and all levels which combine with it to give band nulls. The combination $1S$ - $1P$ was not observed in the band system, because the band head that would result from it is too far in the infrared region for measurement. Consequently the $1P$ level is calculated only from the band nulls of the series $1P$ - $2S$, $3S$, and $4S$, and possibly from assumptions about the X , Z , and D levels that may not be fully justified.

Therefore, considering Curtis' initial P level in the first band system as approximate only, and being doubtful about the other P levels which were found from only one series, $1S$ - $2P$, $3P$, and $4P$, I make the comparisons and suggest the corrections indicated in the following schedule:

<i>Curtis Band Levels</i>	<i>Difference</i>	<i>Doublet Levels</i>	<i>Difference</i>	<i>Corrected Band Levels</i>
29517.25	294.35	29223.88	301.51	29525.39
12795.4	49.32	12746.08	49.58	12795.66
7108.8	14.21	7093.59		
4516.3	6.34	4509.96		

The difference 294.35 is intermediate between the hydrogen differences 291.22 due to $bbab$ - bab and 301.51 due to $bbaa$ - $abaa$, while the difference 49.32 is almost identical with 49.58 due to $bbaaa$ - $abaaa$, all of which are found in Table 1. The addition of one hydrogen atom to $bbaa$ would produce $bbaaa$, according to our formal scheme.

This correction of Curtis' leading level requires a like correction, by the addition of 8.14 to the wave number of each, to all the levels which combine with $1P$ of this system. This correction has been made to all the levels

affected, as set forth on the right-hand side of Table 54, Part 1. We now are able to account for the X and Z levels demanded by Curtis' classification, as follows:

Hydrogen <i>bbb</i>	12988.26	Hydrogen <i>bbbb</i>	7273.20
<i>baa-aaa</i>	248.60	<i>babb-aabb</i>	185.44
Difference	<u>12740.06</u>		<u>7087.76</u>
$2Z$	<u>12742.14</u>	$3Z$	<u>7088.14</u>
Discrepancy	2.08		.38
		Hydrogen <i>abb</i>	12707.51
		<i>bbaba-baaba</i>	166.37 ?
		<u>2X</u>	<u>12551.14</u>

The D level probably is due to a deduction of a hydrogen difference from the helium level 12191.47 or from one of the sub 2 sub 1 levels in Table 1, but I have not completed the tables for hydrogen sufficiently to determine which of these levels should be selected.

In the second band system, as in the first, the combination $1S-1P$ is not within the range of observation, and the $1P$ level is known only approximately, from a single short series of band nulls. The correction required turns out to be greater than in the first band system and much more difficult to discover, because there is no other series separated from the P series of levels by small hydrogen differences. There are, however, several methods of making the correction, the most direct being to identify the $1X$ level of Curtis with the hydrogen level *baa*, of which the wave number is 12435.10. This requires addition of 20.8 wave numbers to Curtis' $1P$ level and to all other levels with which it combines directly to give band heads. The corrected levels are given on the right-hand side of Table 8, Part 2. The corrected initial Z level is then found to be the hydrogen level *abb* less 106.71; this is probably due to *bbaaa-abbb*, which will be found by subtraction from levels given in Table 1 to be 106.09. The discrepancy is not beyond the range of probable error, though it is not sufficiently small to make it certain that some other combination, not resolved in Table 1, may be preferable when the problem is fully solved.

However, that the X level of the second band system should be identified with a level of hydrogen was not the method by which the wave number 28444.2 was discovered to be correct. The discovery was the result of careful analysis of various bands of the second band system which were not accounted for by Curtis in an entirely satisfactory manner, even to himself.

Both Curtis and Dieke published classification of a group of lines in the second band system for the head of which Curtis computed the D level 12040 given in Table 54, Part 2. It is my opinion that the origin of this system was not correctly assigned because two different branches were treated as a single branch. I have rearranged the branches of this group in Table 55, using the wave numbers as given by Dieke, in a manner which shows the band head and the "combination" which produces it. In this

case the line 16252.87 is the head of the band and is due to the combination 28444.2-12191.47, the latter being a level of the regular spectrum of helium. The other branches are accounted for in the table.

Occurrence of a line at a band head where ordinarily a null is expected in classification schemes is not uncommon in helium bands, and there are a few instances of it in the many lined spectrum of hydrogen. Usually such lines are diffuse. In some cases one investigator has reported a line where another has computed a null.

In Curtis' sixth paper, published by the Royal Society in 1929, he gives a group of lines the classification of which he considered doubtful. I have rearranged some of these lines in Table 56 (p. 178) with first and second differences. Each branch, with few exceptions, begins with a line and not a null. The table with notes beneath it gives sufficient analysis to make further comment unnecessary.

Table 57 gives my interpretation of still another group of lines associated by Curtis with his second band system. This band also was classified by Dieke, and the wave numbers in my table are taken from his paper.* The nulls and levels were supplied by myself. The interpretation of these bands, sufficiently indicated in the table, confirms the P level 28444.2 within the range of probable error.

The leading levels remaining for interpretation in both Tables 53 and 54 are those designated S . The regularities of the progressions of the $3S$ and $1S$ series in Table 53 leave no doubt in my mind that the leading levels are due to $c_2c_2c_2c_2$ and $a_2c_2c_2a_2$, respectively. No hydrogen differences are necessary to account for either of these series. The first level of the first band system probably is due to $b_2c_2c_2b_2$. All three series of levels mentioned are due to hydrogen accretions. In the case of the S level of the second band system, it seems to arise from a deduction of a hydrogen difference from the leading $1S$ level of the singlet line system. I have not sufficient check upon the accuracy of the second band S levels to be sure of the difference numbers.

The lines of helium in the visible and adjacent regions are known sufficiently well to make reasonably accurate comparisons such as have been made in the foregoing discussion. In the Schumann region, though much good work has been done, the measurements are not equally precise when expressed in wave numbers, and it is impossible to allocate small difference numbers with precision. Moreover, there are many lines in the Schumann region which have not been measured, or at least for which no measurements have been published. Therefore, although there are connections between the systems known in the visible region and those observed in the Schumann region, these are not known with the precision necessary to evaluate exactly any levels in the Schumann region, or even to make entirely certain what are the combinations with levels given in Tables 53 and 54.

Lyman observed portions of the helium spectrum in the far ultraviolet.

* *Zeit. für Physik.*, 54, 834 (1929).

His lines of the regular spectrum were more accurately measured by Kruger.* In the right-hand column of Table 58 will be found the series limit for helium calculated by applying the simple Rydberg formula to the various lines observed, assuming that this formula would apply to any line. The successive levels thus calculated also are given. The purpose is not to derive a satisfactory series formula but merely to show that the simple formula employed by Fowler must require correction, and to indicate the order of the correction that would be expected. It is clear that the error in using Fowler's levels in Table 52 cannot be large for levels and lines in the visible region, but that there must be errors which make selections of small difference numbers impossible with the data yet systematized.

Lyman also measured a group of lines in the Schumann region which later were measured more accurately by Kruger. These lines are given in Table 59. They are supposed to result from combinations between a level in the Schumann region and the $1P$ series of the visible singlet system given in Table 53. The discrepancies are not greater than are compatible with this supposition. The level 198313 or thereabouts must be accounted for.

In addition to this series there is another series in the Schumann region reported by Hopfield, who gave the wave lengths in Table 60, from which I have calculated wave numbers of lines. These lines are supposed to result from combinations between the levels of the doublet line system of Table 53 with another level in the Schumann region. I have calculated what this level should be if this assumption is correct and have given the result in Table 60, in which it is readily observed that the discrepancies are large and irregular. The average is wave number 151229. It may be significant that there is no line recorded corresponding to a combination with the first $3P$ level. I am inclined to the opinion that this system is due to combinations with the P levels of the first band system, with hydrogen differences which are not the same as with the $3P$ line levels in the visible region; but I do not know that Hopfield's wave lengths are sufficiently accurate to stand precise analysis, and this tentative opinion must be held in abeyance. In any event a level in the neighborhood of 151229 must be accounted for.

I now refer to Table 61 (p. 181), in which I have assembled the leading levels of the principal series that are not modified by deductions of hydrogen differences of small magnitude.

In discussing the development of the many lined spectrum of hydrogen in Chapter 14 it is shown that the difference represented by $b-a = 8076.43$ is important. We might expect from analogy that the difference c_2-a_2 would be of similar importance in the helium spectrum. Since we know a_2 (Table 58) we can find c_2 if $c_2-a_2 = 198313$. This would give for c_2 637225. This is within reasonable expectation of a value of c_2 obtainable by extrapolation from the levels in Table 53. If it is correct, the level of c_2c_2 should lie between $c_2 \div 4$ and $4 \times c_2c_2c_2c_2$, and therefore between $637225 \div 4 = 159306$ and $4 \times 38454 = 153816$, the average of which is 156561. It is my present

* *Phys. Rev.*, 71, 855-9 (1930).

opinion, subject to correction when better data are available, that the level at approximately 151229 is due to $c_2c_2 - (ba - bb = 6048)$, which would make c_2c_2 about 157278, the quantum number of which is .8351. Until more data are available I consider it futile to attempt to evaluate any more levels in the Schumann region, of which it is obvious that there may be a considerable number. Possibly some of these may be evaluated for sub 2 which are not revealed by helium lines, but may be by lines of some other element in which sub-element 2 is an ingredient. Further information about this sub-element will be obtained in Chapter 5, for this sub-element is an ingredient of many of the chemist's atoms.

The atomic volume of helium is 2.36 times that of hydrogen, which suggests that the helium atom is a hydrogen molecule with something additional, which makes it heavier, much more stable and consequently chemically inert. It also suggests that atomic volume is attributable to the structure of ions rather than to the positions of electrons with respect to them.

Objections to the foregoing analysis

Quantum theory and wave mechanics regard helium gas as made of atoms consisting of two electrons revolving about a very small positive nucleus of charge $+2e$ and mass number 4; the nucleus is not divisible by ordinary electron bombardment. This hypothesis is directly contradictory to the analysis that has been developed in this chapter. But this hypothesis was framed before the facts contained in this chapter were known, and it never has taken them into account. Eventually the facts must be acknowledged, no matter what obstacles they may encounter when first brought to light.

The hypothesis that helium has an indivisible nucleus was greatly reinforced by Rutherford's opinion that the alpha particle emitted by radium and other radioactive elements is identical with a doubly ionized helium atom. I have studied Rutherford's papers and am of the opinion that this conclusion is not sound, and I do not think that he would have advanced it if he had been in possession of the information I have just presented. To me his investigations seem to indicate that the alpha particle is very small, has mass number 4 and charge $+2e$, but I do not identify those particles with helium atoms particle for particle.

Rutherford placed a closed receptacle where these particles could penetrate its walls and examined spectroscopically the gas which accumulated within the receptacle. He reported finding helium lines. This established the presence of helium within the receptacle, but not the number, mass or the configuration of the bodies by which the lines were emitted. The determination was qualitative only, and did not deal with individual particles at all. There are several alternatives which can account for the presence of helium without assuming that the alpha particle, having acquired electrons, and undergoing no other change, is helium.

One of these alternatives is that the alpha particle of mass 4 and charge $2e$, taking Rutherford's determination of these attributes as correct, is composed of two sub 2 ions with two electrons binding them together. Such a molecule would be somewhat similar in structure to the hydrogen molecule, but very much smaller, and with a charge of $+2e$. Upon coming into contact with any material containing hydrogen and electrons it could be converted into two atoms of helium, each of mass 4. I do not allege that there is proof of this at the present time. Proof may be forthcoming at some future time if the suggestion is sound, but at present there is no more proof than there is for Rutherford's hypothesis, although the objection to Rutherford's hypothesis is removed.

By positive-ray analysis alone, sub-element 2, singly ionized, would be indistinguishable from the alpha particle if it is constituted as suggested. From theoretical investigations that are referred to in a later chapter, I do not think that the helium atom can be ionized without separation of its sub-atoms.

Information about sub 2 not obtainable from the spectrum of helium is furnished by analysis of the spectra of other elements, as will appear in other chapters, for this sub-element is present in most, if not all, the elements of higher atomic number than 1.

Prediction 1. It will be found that excitation of helium and deuterium together under conditions that must be determined experimentally may result in:

(a) The production of some lines that occur in mixtures of hydrogen and deuterium but not in either element alone.

(b) Lines not found in hydrogen, deuterium or helium or in mixtures of hydrogen and helium. Specifically, the strong line of wave length 6878.149 (Fowler) will have a companion at about 6644.5 and other companions less intense. The strong line of wave length 5875.618 also will have companions.

(c) Hydrogen lines will be more plentiful than in pure helium owing to replacement of hydrogen by deuterium in the development of the modified helium spectrum. Hydrogen may be separated from the mixture after excitation and refined methods of positive-ray analysis will reveal helium atoms of mass number 5.

The precise conditions of pressure and excitation required to produce these effects may be difficult to determine, because of the fact that hydrogen atoms are only half as heavy as deuterium atoms, and segregation is to be expected to take place in the excitation tube. It may be necessary to use very high frequencies and very long tubes viewed end on to make these spectral lines observable, and to recirculate the mixtures through the excitation tubes, with intermediate steps to remove the hydrogen liberated.

Chapter 5

Long First Order Series

There are two chemical groups of elements which yield long series of lines attributed to differences between levels the quantum numbers of which differ by approximately one. These are called first order series, and it was by this criterion that first order spectra were originally judged. The first group is that of the alkali metals, and the second group comprises the inert gases. The members of these groups adjoin one another on the scale of atomic numbers, and their atomic volumes are greater than the atomic volumes of other elements next to them on that scale.

The first order series emitted by the alkali metals have many terms, but the series are comparatively few in number, while the inert gases emit many series with fewer terms. Because of their greater simplicity the series emitted by the alkali metals were among the first classified, much of this work having been accomplished before the advent of the quantum theory. In Fowler's "Report on Series in Line Spectra," published in 1922, both lines and levels are given for lithium, sodium, potassium, rubidium and cesium. He recorded all the lines reported, of which a number were unclassified; one for lithium, five for sodium, four for potassium, three for rubidium and nine for cesium. The levels were calculated by series formulas for the $1s-mp$, the $1p-ms$ and the $1p-md$ series. There were lines classified as due to other combinations, the wave numbers of which did not fit the assigned calculations perfectly, indicating either large errors of measurement of a number of such lines or some defect in the mathematical theory that they are simple differences between unchangeable levels.

Of these combination lines not used in determining the series levels there were in Fowler's report 15 for Li, 26 for Na, 19 for K, 14 for Rb and 8 for Cs. In some cases the correspondences were quite close, but not as close as those of the regular series, but in some cases the differences were quite large, amounting to several wave numbers, far greater than any probable error in measurement. This lack of complete correspondence is mentioned as a caution to be kept in mind in interpreting the physical meaning of levels, and not to disparage the work of those who made the observations.

In this chapter I shall deal with levels only, not with lines, and I shall use the levels evaluated from the longer series, taking the data directly from Bacher and Goudsmitt's "Atomic Energy States," published in 1932, because this is available to most students who are interested in spectroscopy at

the present time. To some of these levels there may be some additions or corrections of more recent date, but they are few in number, and of no special importance for the present purpose.

My purpose is to show that hydrogen is responsible for certain important features of such first order spectra as possess well defined series. This is to be accomplished by comparisons of other first order spectra with hydrogen and helium spectra and with differences evaluated in the analysis of the hydrogen secondary spectrum, in much the same way as the connections between the hydrogen spectrum and the helium spectrum are revealed in Chapter 4.

Lithium

Lithium is reported by Aston as having about 91.7 per cent of its atoms of mass number 7, packing fractions not considered, and 8.3 per cent of mass number 6. I am of the opinion that the regular series of lines of lithium are due to Li 7. On this hypothesis the entire regular first order spectrum may be accounted for satisfactorily. The atomic number of Li is 3. If the scheme used in accounting for hydrogen and helium is to be extended, we must assign to lithium one sub-atom of atomic number 3. My analysis will show that we must also assign to it sub-atoms 1 and 2. This leads to the suggestion that one of these sub-atoms must be isotopic. It cannot be hydrogen, for there is no evidence of deuterium in the spectrum of lithium. It is not likely to be sub 2 because no stable isotope of helium of mass 5 or mass 6 is known. Therefore it is most probable that the sub-element which is isotopic in Li is sub 3, and I will designate these isotopes of sub 3 by 3_s and 3_4 when it is necessary to distinguish them.

In Table 62 (p. 182) the levels are those evaluated by Fowler, from the longer series, and I attribute them to recombination products of the sub-atoms composing Li 7, sub 3_s being so small in amount as not to have left any record intense enough to be observed by the methods employed.

On the right-hand side of Table 62 are the levels of lithium, and on the left-hand side levels of helium for comparison. The first thing to be noted is that the initial d level of lithium differs from one helium d level by only 2.68 wave numbers. In discussing helium we found it necessary to shift all the levels of one of two separately classified systems in order to show the relationships between the two systems with precision. This does not involve making any changes whatever in the wave numbers of lines or in their classification. It may be that these two levels, found independently by different series formulas which at best are approximations only, ought to be identical. Whether the shift should be entirely in lithium, partly in lithium and partly in helium, or entirely in helium, cannot be determined by comparison of these spectra alone. I will therefore, for the sake of making comparison, add 2.68 wave numbers to the d levels of Li, and compare them with levels which are given in Table 52 (p. 175) due to molecules composed of atoms of hydrogen combined with ions of sub 2.

<i>Lithium, corrected</i>	<i>Hydrogen-sub-2 levels</i>
$12203.1 + 2.68 = 12205.78$	12205.78 $a4a_2$
$6863.5 + 2.68 = 6866.18$	6866.17 $2a2a_2a$
$4389.6 + 2.68 = 4392.28$	4392.52 $2a2a_2a_2a$

The *f* levels of Li may then be accounted for as due to deductions of small hydrogen differences from other levels of Table 52 as follows:

<i>Lithium, corrected</i>
$6856.1 + 2.68 = 6858.78 = 6864.29 - 5.51$ or $6866.17 - 7.39$
$4381.8 + 2.68 = 4384.48 = 4388.93 - 4.45$ or $4390.69 - 6.21$

The differences 7.39 and 6.21 are very close to second differences of the *Q* series in Table 3. It must be remembered that the hydrogen differences evaluated from the measurements of Gale and associates in 1928 are more accurate than Fowler's measurements prior to 1922.

In comparing the *p* levels of lithium with levels of helium we find that they differ but slightly from *p* levels of Curtis' second band system, given in Table 54. The differences given in Table 62, even if corrected by adding 2.68 or any other number to the levels of Fowler, do not prove equal to a sufficient number of hydrogen differences to make it acceptable to assign these to the same origins as difference numbers in the secondary spectrum of hydrogen.

In the chapter on helium the level 28444.2 was assigned to $a_2b_2b_2a_2$ and not to $a_1b_2b_2$. This was done as a result of analysis of helium only, before I had attempted to account for Li I. I see no reason for changing this classification. The initial *p* level of lithium is assigned to $a_1b_2b_2$, by extrapolation of which we can find, approximately, the level b_2b_2 , which is done in Chapter 6, interpreting the second order spectrum of lithium. If that level combines with the first order *s* and *d* levels of Table 62, the lines would be in the Schumann region, and are not included in the first order spectrum of lithium classified by Fowler. The helium band series and the lithium line series both are true first order series. In both cases the accretions are due to hydrogen.

The *s* series of levels are the only ones that can be ascribed to molecules containing sub-atom 3. The successive levels after the first are due to hydrogen accretions, if this general scheme is applicable, for which good physical reasons must be found before the scheme arises to the dignity of a theory. I have ascribed the initial level to $asx'as'as'as'sas$, using the symbol x' to designate a configuration of sub-ion 3, which will be further discussed in connection with the spectrum of neon in this chapter and of the enhanced spectrum of lithium in Chapter 6.

Another feature of this spectrum which may be of importance in giving it physical interpretation is the fact that the *s* series of levels has but six terms, while the *p* series has 41 terms. This might be due to the order in which the lithium atom is disintegrated by excitation. It would be expected that the hydrogen atoms would be the first separated, leaving the

sub 2 and sub 3 atoms joined, with more than two electrons binding. Further ionization would then liberate sub 2 ions with one electron only, leaving sub 3, which would have to lose one of its remaining electrons before it could enter into such combinations with other ions as are required by the schedule in Table 62. This is a rather stringent requirement, which must be met in the second part of this book if this scheme is to have theoretical justification consistent with the fundamental principles of mechanics and electromagnetics. The numerical relationships set forth in Table 62 are quite independent of any interpretation that may be placed upon them. They are facts, which must be acceptable to any rational theory.

If, however, the atom is made up of three sub-atoms as outlined, the hydrogen would be further separated from the sub 3 atoms than from the sub 2 atoms, and the longer *p* series would be expected as a natural consequence.

Sodium

The first order levels of sodium are given in Table 63 (p. 183). Comparison of them with those of lithium in Table 1 reveals the fact that both *d* and *f* levels of sodium are of larger wave number than those of lithium and the *s* and *p* levels of smaller wave number. It also will be noticed that the *p* levels of sodium are doublets of quite small separation, suggestive of the separations of helium-hydrogen levels in Table 52, but not identical therewith. Similar separations also will be found in the spectrum of neon, to be discussed later in this chapter.

The evidence from the analysis to follow, interpreting Table 63, is that the first order sodium spectrum is emitted by recombination of sub-atoms 1, 2, and 3 only, sub-atom 11, the atomic number of sodium determined by x-ray spectra having no part whatever in its development, except such as it may exercise upon the order or manner, or combinations, in which the sub-atoms of small atomic number are liberated. This of course would affect the probable recombinations into which they would enter.

In discussing the first order spectrum of lithium, represented in Table 62, I attributed the *s* levels to molecules containing sub-ions 3 of mass 4. The initial *s* level of sodium is of smaller wave number and well may be attributed to the corresponding molecules containing sub 3 of mass 3 which, from analogy with the levels of deuterium and hydrogen, ought to be less than the levels of the heavier isotope, and perhaps considerably less.

The *d* levels of sodium are all too large to be attributed to combinations of sub 1 and sub 2, as in the case of lithium, but may well be accounted for as due to similar combinations in which sub 3 in the *a* configuration plays a part. I have so accounted for them in the table. The quantum numbers of the *p* levels are accounted for as involving molecules in which sub 3 also plays a part. However, there is positive evidence in this spectrum of presence of sub 2 in the fact that the *p* levels are doublets of small separation, though both series are true first order series. There is a second order

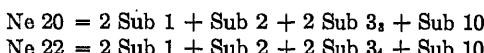
spectrum reported for sodium, but in it there are no long well developed series and no "absolute" levels have been evaluated. These facts seem to indicate a scarcity of sub 2, but not its absence. At any rate, sub 3 plays a much more important part and sub 2 a less important part in the formation of the molecules to which I have tentatively assigned the levels of sodium than in the formation of the molecules responsible for the lithium spectrum.

In sodium, long series indicate abundance of hydrogen, as does the fact that hydrogen primary lines accompany the sodium first order spectrum. The atomic volume of sodium, 1.929 times that of hydrogen, seems to indicate the probable inclusion of two atoms of hydrogen.

The first order spectra of other elements of this chemical group are similar to that of sodium except that there are doublets among the *d* levels as well as the *p* levels. In the x-ray spectrum of potassium, however, there is ample evidence of the presence of sub 4, and I have not analyzed the levels of any of these heavier elements as I have for lithium and sodium.

Neon

Mass spectroscopy has shown that there are three stable isotopes of neon, which have mass numbers 20 (90 per cent of the atoms), 21 (.27 per cent) and 22 (9.73 per cent). The commoner forms may be accounted for as follows:



Thus each atom of neon contains the equivalent of one helium atom, two atoms of sub 3 (both isotopes being represented) and one of sub 10, and although it is usual in neon for both atoms of sub 3 to be alike, there are some in which both isotopes are present in the same atom. If this analysis is correct, when neon is broken under excitation it would be possible for both isotopes of sub 3 to be present in recombination products which form in the excitation chamber. In my opinion it is due to this that there are "offset" series in the spectrum of neon. Neon thus contains all the sub-atoms necessary to account for the spectra of helium and the first order spectra of lithium and sodium (Fowler). Yet the lines of helium and lithium and sodium do not accompany the lines of neon, or if they do, are attributed to impurities. This will have to be accounted for if the system here proposed is sound.

The first order spectrum of neon is unique in several respects. It is the first spectrum classified with "offset" levels, and the verification of the classification, which was accomplished by Paschen with the aid of series formulas, does not depend in the slightest degree upon those formulas, but is established by the complete balancing of the system within itself, in much the same manner as my table for hydrogen (Table 1) balances because there are so many intercombinations involving the same levels. For many classified spectra, this is not true, particularly for spectra for which only "relative" levels have been evaluated.

While none of the series of neon are very long, like the long series of the alkali metals, they are long enough and regular enough to make possible the calculation of series formulas with considerable precision, and there are many series of levels — 22 in all. They contain too many terms to include all of them in a discussion of this kind, and in the tables I have given only the first five terms of each series, one table for the *s* levels, one for the *p* levels and one for the *d* levels. While the wave numbers are taken from Bacher and Goudsmit's compilation, I have referred to the original papers by Paschen for the classification of the lines and their analysis. From Paschen I learn that the balancing is not perfect in an absolute sense when lines, not calculated levels, are considered, there being discrepancies larger than probable errors in measurement. This, however, does not invalidate the classification scheme, although it has a bearing upon the final interpretation of the levels, which may perhaps not be physically and absolutely constant. This would seem to be likely if they are derived from interaction of more than one molecule. This, however, is a matter to be considered in interpretation, not in classification.

The lines classified by Paschen are combinations of the $3p$ levels of Table 65 with both *s* and *d* levels of Table 64 and 66 and combinations of the initial *s* levels of Table 64 with the *p* levels of Table 65. No combinations of *s* and *d* levels are found. In the spectra of lithium and sodium the *s* levels are singlets. In the case of neon there are four distinct series of *s* levels, two of which follow a modified Rydberg-Ritz formula, and two "offset" from a calculated regular formula by approximately constant but not truly constant difference numbers. Those designated s_5 and s_4 converge, the differences between terms diminishing with regularity. The differences between term wave numbers are given in Table 64 for comparison, and they are found to be almost identical with hydrogen differences recorded in Table 1, at least so far as the larger difference numbers are concerned. This feature is similar to the difference system found between line and band levels of helium in Chapter 4.

The offset *s* levels are designated s_3 and s_2 . In Table 64, I have compared them with the corresponding s_5 levels, giving differences. These differences cannot possibly be identified with hydrogen differences in Table 1. The only satisfactory explanation of them that I have been able to think of is that they are due to the presence of both isotopes of sub 3 in the line molecules responsible for them, this rendering the line molecule unsymmetrical; the series therefore approaches a limit which is not zero by somewhat irregular steps. It must, however, be remembered that the number of lines in any observed *p-ms* series is limited and comparatively small, varying from five to twelve as recorded by Paschen. In my opinion the number of terms possible to excite in any first order series is limited by the amount of hydrogen in the *a* configuration present in the material excited, and by the demands for it in other series. This also would account for the well known fact that in excitation of long first order series the hydrogen primary lines

which accompany the lines ascribed to other elements are stronger upon initial excitation than after the excitation has been prolonged. The hydrogen is gradually appropriated in extending the other series.

In ascribing molecular origins to the levels of neon I have used the same symbols, x and x' to designate the isotopes of sub 3 as in the tables for lithium and sodium. If, as is assumed in accounting for the prevalence of the isotope of mass 22 over that of mass 21, it is usual in neon for both atoms of sub 3 in any atom of neon to be of the same mass number, those like atoms liberated from one neon atom would be more likely to recombine with one another, or to remain combined in case they were not separated from one another in being liberated from No. 10. In this case the combination xx would be more common than the combination $x'x'$, or either of the combinations $x'x$ or xx' . When two such line ions combined with one another, the more probable form would be $xxxx$, and the least probable $x'x'x'x'$. Of the six other forms mathematically possible $xxx'x'$ would be the most likely. There might also be atoms of sub 3 in the a configuration, of which the form a would be much more likely than a' ; but by analogy with hydrogen and deuterium the form a' would have a wave number only slightly larger than the form a , although a much larger difference between the forms x' and x would be expected.

The lines due to combinations of the less likely levels would in any event be very much feebler than those due to the more likely levels, and they may be entirely absent, or so lacking in intensity as to escape observations such as hitherto have been made. I have ascribed the levels in the tables to those line molecules which to me, as at present advised, seem most likely from the spectroscopic observations. Again, let it be remembered that what I consider important and requiring interpretation are the numerical relationships revealed in the tables, which constitute data. My own interpretation is introduced only for the purpose of showing that the data are consistent with it. The data may also be consistent with some other scheme, but I have not been able to reconcile them with quantum theory.

In Table 65 the p levels of neon according to Paschen are compared with one another and accounted for. The p_{10} levels are separated from corresponding p_9 levels by hydrogen secondary spectrum differences, the larger of which are found in Chapter 2. This also is true of the p_8 and p_7 levels. These four series of levels can be expressed approximately by a modified Rydberg formulae. The p_6 and p_3 levels are placed opposite one another in the table for comparison. They both are fairly regular first order series, but the difference numbers by which they are separated are not hydrogen differences, as are those of p_{10} and p_9 and p_8 and p_7 . These parallel series are explicable as due to the presence of one atom of hydrogen in the line responsible for the initial level of p_6 and two atoms of sub 2 in the line responsible for the initial level of p_3 .

The other four series of levels in Table 4 are offset, by amounts approximating the separation of the s_5 and the s_3 levels, indicating some common

property in the origins. I have suggested origins at the bottom of the table, which must at present be regarded as provisional, subject to correction when more data are available or more study has been devoted to the problem, which ought to be after some mathematical and theoretical justification has been developed to account for, and perhaps also to correct, the general scheme which has been followed in this presentation.

Table 66 gives a comparison of the *d* levels of neon. There are eight series which may be represented by formulas of the ordinary kind, and four which are offset, which Paschen originally designated as $s_1's_1''s_1'''$ and s_1'''' , but they are true *d* levels, though offset. Beneath the table proper I have given symbolically my interpretation of the origin of the leading member of each series. The presence of offset series of levels in all three groups of levels of neon indicates some property in the origins of the regular and the offset series which are common to all groups. This, in my opinion, must be ascribed to the fact that sub-element 3 is isotopic, both isotopes being present in neon.

The first order spectra of argon, krypton and xenon are similar to that on neon in general structure, all of them having offset series.

Does the scheme of ascribing the various levels of the elements considered to line molecules of sub-elements differing from the original atoms from which they are derived give any suggestion as to why hydrogen lines are the only ones of appreciable intensity which these elements have in common? Since all the sub-elements necessary for all of these spectral lines are present in neon, why is not the spectrum of neon accompanied by lines of sodium, lithium, helium, as well as the few lines of hydrogen, which are known to be present on initial excitation, and not removable by any method of chemical purification?

The answer must be that although the requisite sub-elements are present in neon, they are not present in the most favorable proportions, and perhaps are not liberated in the configurations favorable for the formation of the molecular combinations necessary, directly or indirectly, for the production of the lines from which, by the usual methods of analysis, the levels are evaluated. Moreover, it is possible that some lines ascribed to other elements actually do occur in neon, suitably excited, but are so faint as not to have been observed, or have been ascribed to impurities.

The reader may be interested in knowing why, in discussing first order series, I have skipped from atomic number 3, lithium, to atomic number 10, neon, instead of proceeding in regular order of atomic numbers and discussing first order spectra of beryllium, boron and carbon after lithium.

I would have followed that order if there were *long* first order spectra of the three elements mentioned, excitable with the chemically pure elements, in the vacuum arc. Such, however, is not the case.

A few predictions may be ventured based upon the subject matter of this chapter in connection with that of chapters 1, 2, 3, and 4.

(1) If Li 6 is isolated from Li 7 in sufficient quantities to make possible the investigation of its spectrum independently of that of Li 7, it will be found that the *s* levels of Li 6 are identical with those of Na.

(2) When the concentration of Li 6 in connection with Li 7 is greatly increased, there will be found offset levels among the *s* levels of Li but not among the *p* levels, in the production of which sub 3 has no part.

(3) When either Ne 20 or Ne 22 is obtainable in approximate purity without the other, there will be no offset series producible in either pure isotope alone.

(4) Mixtures of neon and deuterium may be so excited as to yield lines not present in either element alone.

(5) In the products formed after such excitation the number of atoms of mass number 21 may be increased over those in normal neon, but their exact mass numbers will not be identical with the mass number of the present known isotope of gross mass number 21, the packing fractions being somewhat different. Some atoms of mass number 23 may also be found due to the substitution of deuterium for hydrogen in normal Ne 22.

Suggestion: It would be worth while for an examination of the fainter lines associated with the classified lines of neon to be studied critically, with apparatus of greater resolving power than that available to Paschen when he analyzed this spectrum, to ascertain whether some of these faint lines may not be identical with band lines of helium or hydrogen, or atomic lines of helium, sodium or possibly lithium. This would be a very arduous task, both as to observation and comparison.

Chapter 6

The Interpretation of Spectral Orders

The first series formula, that of Balmer, which was extended later to include more than one series and thus became the simple Rydberg formula, was originally suggested by the very obvious regular spacing of the Balmer lines of the hydrogen spectrum. It was not devised as interpretive of any theory about the origins of the causes of the lines. The interpretation given to the Rydberg formula by Bohr and the discovery that this simple formula did not represent the relationships of the wave numbers of the lines exactly, but only approximately, and that there is "fine structure" in at least some of the lines, led to modifications of the simple formula for two purposes, one to express the observed relationships more accurately, and the other to conform more closely to the mathematical implications of the theory. Modified Rydberg formulas intended to account for other types of spectra have been subjected to the same kind of treatment, partly to express observations more exactly, and partly to agree with mathematical theory. They have not succeeded in doing either with absolute perfection, but they have been exceedingly useful in the work of classifying spectral lines, small discrepancies being disregarded.

In actual practice several lines supposed to belong to a regular series are used to calculate approximately wave numbers of a series of levels and of a single level between which and the calculated series the wave numbers of the observed lines are arithmetical differences. The single level is thus determined as accurately as possible, and the other levels are then determined with precision with reference to that level by simple subtraction. Thus, if there is some error in the determination of the one level, all other levels of the group or system are equally in error. The error may be detected if it is possible to compare any of the levels of the system with some level of another system more accurately known, and the difference between the levels compared also is known. This is the method I have employed in correcting the various independently classified sub-systems of helium with respect to one another in Chapter 4, and in correcting the lithium spectrum for comparison with helium in Chapter 5.

The levels to which series formulas apply directly, and which may be calculated with great precision by series formulas hitherto considered in Chapters 2, 3, 4, and 5 are called first order levels. They are distinguished from levels of other orders which are also related to one another by series formulas by the simple fact that their quantum numbers, when arranged in

serial order, differ from one another by numbers that approximate more and more closely to 1 as the term number increases. Levels which are determined in this way are called "absolute," to distinguish them from levels which are expressed merely as differences in wave number from another level the actual wave number of which is unknown. Such difference numbers are called "relative" levels, and are used in classifying many spectra for which no series formulas are known, and for preliminary work in classifying spectra for which series formulas and absolute levels may later be found.

There are spectral systems which may be classified by the use of series formulas in which the quantum numbers differ by approximately 0.5 and others in which the quantum numbers differ by 0.333, or very nearly that. These are called second order and third order spectra, and the levels also are called absolute when so determined. In this connection the word "absolute" does not mean "exact," but only that the attempt has been made to obtain as true values as practicable.

For the first 36 elements considered in order of atomic numbers, absolute levels are known for first order spectra of 23, only relative classifications having been made for the other 13. For the same elements there are but 12 for which absolute second order levels have been calculated, 24 remaining in the relative stage of classification. The methods employed in making relative classifications will be shown later in this chapter for our purposes of indicating the presence of sub-elements 1 and 2 in chemical elements of other atomic number. Here it will be more appropriate to show how analysis of second order absolute levels contributes to the analysis of the chemical element from which, by suitable excitation and all of the changes that result therefrom, the second order spectrum is derived.

The Spectrum of Li II

The second order spectrum of helium has been discussed in Chapter 4. It is a simple spectrum like that of the primary of hydrogen, but of about four times the frequency. Next in order on the scale of atomic numbers is lithium, the first order spectrum of which is discussed in Chapter 5, the levels given in Table 62 (p. 182), to which it will be convenient to refer while discussing the second order spectrum for which levels are given in Table 67. Those levels were calculated by Werner and Schüler (1926 and 1927). The analysis indicated in the table shows that the same sub-elements contribute to the second order series as to the first order series, but in a different manner. The progressions by quantum number are by accretions of approximately 0.5 instead of 1. There are two *P* series and two *D* series instead of one of each, as in Li I, and there is a singlet *S* level in the Schumann region; all the levels thus far mentioned originate in molecules composed of sub 2 and sub 1 atoms only, modified by hydrogen differences which are identified in the table.

As in the first order spectrum the *S* series, which has six terms, is the only

one in which sub 3 plays a part. Its leading level, wave number 134033, for which the quantum number is 0.9046, is attributed to the molecule $x'sx'sx'sx's$, in which $x's$ has the same significance as in Chapter 5, where the initial s level is ascribed to the molecule $a_3s'x'sx'sx'sa'_3$, the quantum number of which is 1.5881. The difference between these quantum numbers is 0.6835, or twice 0.3417, and this is about what ought to be expected to result from the accretion of two a_3 atoms to the molecule $x'sx'sx'sx's$. The progression of the s levels is caused by accretions of sub 2 atoms in the a configuration.

The $3P$ levels are derived from a series of line molecules containing sub-atoms 2 only. These molecules are completely analogous to the series of molecules responsible for the alpha, beta, gamma 0-0 band levels of hydrogen (Tables 3, 17 and 18), the difference being that sub 2 atoms are substituted for sub 1. This regular series does not appear as a series in helium; but one member of it does occur — that of wave number 28444.2 due to $a_2b_2b_2a_2$, the leading level of the P series Table 54, Part 2; this is also given in Table 61. In helium the progressions beginning with this level are due to accretions of hydrogen atoms, but in Li II this level is the third member of a series beginning with b_2b_2 and progressing by accretions of sub 2 instead of sub 1 atoms. The levels evaluated in Table 67 are deductions of hydrogen differences from this regular true series, which follows a Rydberg-Ritz formula. I have calculated the true series approximately, assuming regular progressions of quantum numbers suggested by the helium spectrum. Some corrections may be necessary, for I have not made any shift in the systems of levels calculated by Werner and Schüler. I do not think that there can be any large error in their levels, chiefly because of the regularity of the progressions of the quantum numbers of the S series and the comparatively large number of terms in that series.

The P levels are derived from the regular series of He II given in Table 52, by hydrogen deductions, probably as indicated in the table. In this case the series determinable with the aid of quantum numbers is fully known, and I have used the levels calculated by Fowler. The correspondences are very close, indicating that there can be no serious discrepancy between the data of Fowler and that of Werner.

The D levels apparently are due to hydrogen accretions to levels of the regular spectrum of helium, but some of them may originate in levels due to molecular line combinations of sub 2 and sub 1, alternate members of which are given in Table 52. The hydrogen differences in this case and that of the F levels are too small to be assigned to definite hydrogen combinations of Table 1.

The F levels of both series are due to deductions of hydrogen differences from levels which either appear or should appear in Table 52 or should appear there if that table were complete. This is another case in which levels due to combinations of sub 1 and sub 2 which are not discovered in the helium spectrum can be obtained from spectra of other elements, and

thus assist in the completion of the analysis of helium itself; but, to be used in calculations, this kind of data must be more precisely determined than the present measurements and analyses permit.

Beryllium, Boron and Carbon

We now turn our attention to the spectra of beryllium, boron and carbon which were passed by in discussing long first order series in Chapter 5 because they do not produce such series. In fact, they do not produce first order series at all unless assisted by some other element in the excitation chamber, either introduced purposely to assist in striking an arc, in which case helium seems to be preferred, or as in an impurity in the electrodes, or because the beryllium or boron to be excited is in the form of a salt, in a carbon electrode. But sub 1 undoubtedly is present when first order spectral series ascribed to these elements are developed.

The three elements under consideration are unique in that their atomic volumes are least of all chemical elements. If the atomic volume of hydrogen is taken as 1, that of beryllium is 0.421, of boron 0.403, and of carbon 0.299.

First, second, third and fourth order spectra are reported for beryllium, these orders and also a fifth for boron, and all five orders and a sixth for carbon, although not all of these are satisfactorily known. For boron the only order considered satisfactory from the standpoint of present theory is the third. For beryllium the first and second, and for carbon the first, second and third are regarded as satisfactory, the levels having been evaluated in absolute terms. If all the orders reported implied that a sub-atom corresponding to that order must be present in every atom, the atomic mass of beryllium would have to be not less than 11 instead of 10, of boron 15 instead of 10 and 11, and of carbon 21 instead of 12. If the scheme I am presenting is sound, either some of these reported orders are attributable to some other element or to some impurity, or some of these elements have atoms made up of sub-atoms of different atomic numbers, although the total masses are the same.

To form a just opinion about these possibilities, one must study the original papers of the investigators who made the measurements, and ascertain just what materials they used, and how they made their experiments. Calculated levels are not sufficient. I have not been able to make as thorough a study along this line as I wish, but from what I have been able to find I am convinced that in every case the first order series reported have been developed with the help of hydrogen derived from some other source than beryllium, boron or carbon.

From study of the levels recorded by Bacher and Goudsmit, even with the data being unsatisfactory for several spectral orders, I think that the following conclusions are justified.

Beryllium, mass number 9, no known isotopes, contains sub 4 in some of its atoms. Whether this is of mass number 4 or 5 I have not been able to

determine. If of mass 5, there must be atoms made up of sub 2 + sub 2 + sub 4₅. This would be expected from analogy with lithium, but it does not account for the third order spectrum of beryllium. Sub 3, necessary to develop a third order series, might be derived from carbon electrodes. If it is truly a constituent of some beryllium atoms, there are two possibilities. One of these is that some beryllium atoms are composed of sub 2 + sub 3₃ + sub 4₄. The other is that there are atoms of beryllium which do not contain sub 4, but might be made up of sub 2 + sub 3 + sub 3₄. This would mean that in all cases the chemical properties do not necessarily depend upon the atomic number. My studies have not enabled me to differentiate between possible isotopes of sub 4, and therefore I am mentioning these possibilities, though to some they may seem farfetched. I think that more knowledge will resolve this quandary, and we do not need to settle it by guess.

Boron. Considering the position of boron on the scale of atomic numbers, our knowledge of its spectrum is most unsatisfactory. About 20 per cent of the boron atoms have mass number 10, 80 per cent mass number 11. With the meager spectroscopic data available and doubt as to what other chemical matter might be associated with the boron under excitation, I can only state the possibilities of accounting for these reported orders and also the mass numbers. The possibilities of various structure seem to me to be:

- (a) Sub 2 + Sub 3₃ + Sub 5₆ = B₁₀
- (b) Sub 2 + Sub 3₄ + Sub 5₆ = B₁₁
- (c) Sub 2 + Sub 3₃ + Sub 5₆ = B₁₁
- (d) Sub 2 + Sub 2 + Sub 6₆ or 6₇ = B₁₀ or B₁₁

Carbon. Although two stable isotopes of carbon are known, of mass numbers 12 and 13 respectively, the latter is present in about one-quarter of one per cent of the atoms of normal carbon and cannot contribute appreciably to the observed spectra. The second, third and fourth order spectra of carbon are well established, with absolute values of levels which must be at least approximately correct. The fifth order is very imperfectly known, and it is doubtful if carbon contains any atoms of sub 5. There can be no doubt that it contains sub 2 and sub 3.

Carbon has displaced terms, similar to the displaced terms of neon, but much more difficult to account for because the progressions of quantum numbers in the first and second order spectra are very irregular. This strongly suggests the presence of isotopes among the sub-elements in C₁₂, and the scarcity of C₁₃ suggests that there must be more than one form of C₁₂.

With the data available my best guess is that the commoner atoms of carbon are composed as follows:

$$\begin{aligned} \text{Sub 2} + \text{Sub 3}_4 + \text{Sub 6}_6 &= C_{12} \\ \text{Sub 2} + \text{Sub 3}_3 + \text{Sub 6}_7 &= C_{12} \end{aligned}$$

and that the rare stable isotope is composed of

$$\text{Sub 2} + \text{Sub 3}_4 + \text{Sub 6}_7 = C_{13}$$

The possibility that there may be atoms having the chemical properties of carbon and mass number 12, but with sub 5 and not sub 6, is not eliminated by examination of the spectral levels now attributed to pure carbon. The levels of the fourth and fifth orders, doubtful as they may be, do suggest the possibility of atoms with sub 4 and sub 5 in their structures. These might be

$$\begin{aligned} \text{Sub } 2 + \text{Sub } 4_4 + \text{Sub } 5_6 &= C_{12} \text{ or} \\ \text{Sub } 2 + \text{Sub } 4_5 + \text{Sub } 5_5 &= C_{12} \end{aligned}$$

From investigations in other fields than spectroscopy there are reported atoms having the chemical properties of carbon, but mass numbers 10, 11 and 14, these being unstable. The spectra which unstable forms of carbon might emit, if they were sufficiently plentiful, and concentrated free from other types, are unknown. These forms are identified by their chemical properties in association with other atoms, and by their mass numbers. Their occurrence, however, is not contradictory to the hypothesis that chemical atoms are complex, but rather indicate that the chemical properties of an atom may depend upon the physical structure, and not always upon the atomic number, as that would be determined spectroscopically if possible to obtain the isotope alone.

The present ideas about interpretation of spectra of higher orders are based upon the assumption that atoms are not divisible into component parts, such as considered in my work, but with undivided nuclei are capable of various degrees of ionization, and of emitting spectra of different orders as a result of such ionization and further excitation.

The present state of spectroscopic knowledge according to this conception of the origin of spectra was summarized by Dr. Meggers in the *Journal of the Optical Society* for August, 1946, in the following words: "Since each chemical element can emit as many spectra as it has electrons, the total number of possible spectra for the 92 elements is summation 92, that is, 4278. . . . Briefly, at the present time regularities have been detected in 445 spectra, and of these only 101 are in a state of practically complete description and interpretation." He then gives tables indicating the degree of completeness of classification for the various orders expected for each element in accordance with this scheme, which is the "orthodox" scheme in common use.

In keeping with this scheme all lines ascribed to any spectral order of any one element ought to be capable of classification in a single self-consistent schedule, which would reveal the levels between which the individual lines are differences. As an example, for nitrogen, atomic number 7, there should be seven systems, and only seven. Since, however, not all groups may be within regions which we are able at this time to investigate, or which for any reasons have not been studied or classified, there may be several partly classified groups assigned to a given order, the relationships between which are unknown. In the case of nitrogen Bacher and Goudsmit (1932) give no absolute levels for spectra of higher order than 1. For N II there are two

independently classified sub-systems, for N III three, for N IV three and for NV one, but none for N VI or N VII. It is imperative that the absolute levels of these different spectral groups be found before any interpretation placed upon them can be either sustained or shown to be inconsistent with the data.

If the scheme which I have applied to the analysis of spectra is followed, the number of different separately classifiable spectra which might be obtained from any chemical element is not the same as assumed by the current theory. It would depend not upon the degree of ionization of the atom as a whole, but upon the number of varieties of sub-atoms in its structure, and their capacity for combining with one another in linear formations such as have been indicated in the discussions hitherto. Aside from such evidence of the possibility of such combinations as the numerical relationships revealed by this kind of comparative analysis affords, the scheme which I have used, although amenable to mathematical treatment, is not based upon any preconceived mathematical theory. It is, however, sufficiently fruitful to justify its use for the purpose of extending data that must be accounted for by any satisfactory theory of the origin of spectral lines, and of the structure of those bodies responsible for the lines.

Relative classification of spectral lines without evaluation of absolute levels is possible because there are groups of lines the several members of which are separated from one another in wave number by the same differences. Such groups are doublets, triplets, quadruplets, or even multiplets of more terms. When such groups were compared it became obvious that they might be accounted for as due to combinations of levels separated from one another by the differences observed with several other levels, in which case the separation of the other levels might be obtained by simple subtraction. Following this simple lead, complicated spectra containing multiplets of constant separation were found amenable to relative analysis, and rules were found indicating what kinds of combinations are likely. These rules, empirically discovered, have been adopted into theory. They were by no means predicted in advance of their discovery, nor are the wave numbers of the separations calculable in advance. All of the knowledge we have of these separations is derived from observation.

I have found by comparing the separations of multiplets as recorded in the tables of Bacher and Goudsmit that many of them are identical with differences between pairs of levels evaluated in the analysis of the spectrum of hydrogen, in Chapter 2. Others probably are compounded differences, in some cases due to hydrogen alone, and in some to molecules composed of both sub 1 and sub 2, and some may even be due to sub 2 alone. Of the combinations some may be accounted for when the analysis of the secondary spectrum of helium is complete, using the data supplied by Curtis and Dieke. If my interpretation of these differences is correct in kind, however much it may lack in detail at the present time, multiplets in so-called atomic spectra are not due to properties of atoms as atoms, but to the presence of combina-

tions of levels differences similar in character to those which result in band structure in the secondary spectrum of hydrogen, discussed in Chapter 2, many of which are found in Table 1.

By way of examples, I here give a few of the differences recorded as between levels designated $j = 0$ and $j = 1$ or $j = \frac{1}{2}$ and $j = 1\frac{1}{2}$ in Bacher and Goudsmit's "Atomic Energy States." These all are from P levels of first order spectra.

<i>At. No.</i>	<i>El.</i>	<i>Difference</i>	<i>Hydrogen differences — Chapter 2</i>
19	K	157.71	probably <i>bbbaa-babaa</i>
		19.69	<i>baaa-baab</i>
37	Rb	237.6	<i>baaa-aaaa</i>
		77.5	<i>bbaaa-babba</i>
55	Cs	554.0	<i>bbb-baa</i>
		181.1	<i>aaaab-babbb</i>
29	Cu	248.38	<i>baa-aaa</i>
		58.3	See Table 17
12	Mg	19.9	<i>baaa-baab</i>
20	Ca	52.3	<i>babbb-aabbb</i>
38	Sr	186.8	<i>babb-aabb</i>
		41.4	<i>baaab-aaaab</i>

Chapter 7

X-Ray Spectral Lines

On December 20, 1913, Bohr delivered a lecture in Copenhagen in which he advanced a theory which accounted for the primary lines of hydrogen as due to transitions of electrons from one dynamically stable state to another, with emission or absorption of energy that must be lost or gained by such transitions when the states are not stable. These transitions which resulted in the primary spectrum of hydrogen were assumed to take place in atoms which are uninfluenced by other atoms, and not in molecular combinations. The assumption of stable states of this kind was acknowledged to be contrary to the principles of electromagnetism applicable in other fields.

Bohr's assumptions enabled him to find a formula expressing a mathematical relationship between Planck's constant and the Rydberg number, involving also the mass and charge of the electron and the velocity of light. In the same lecture he also explained the hydrogen-like regular spectrum of helium as being due to changes in stable states in an atom of mass 4 and charge $+e$ when possessed of only one electron of a possible two. He also stated that similar spectra were to be expected from atoms of larger nuclear charge, when deprived of all electrons but one. This initial theory of Bohr was truly mathematical, whatever may be thought of the assumptions upon which it was based.

In 1913, quite independently of Bohr, Moseley announced the discovery of x-ray spectral lines in the regions where the regular spectra predictable by Bohr's theory were to be expected. The x-ray lines, however, did not have relationships to one another of a mathematical kind resembling the anticipated lines, and seemed to bear no relationship to them. In this chapter I shall show that x-ray lines may be accounted for on the hypothesis that Bohr's formula for expected lines was not far wrong, but that the expected lines are not observable because they are modified and converted into x-ray lines by a process analogous to that which is responsible for band lines in other spectra.

In April 1920 Bohr delivered a lecture in Berlin, in which he extended his theory to account for spectra emitted by atoms in which more than one electron is present. This extended theory, while set forth in mathematical terms, was not a mathematical development of the theory propounded in his lecture of 1913, in the sense of enabling him to predict any more spectral lines. It provided a *schema* by which lines could be classified, which proved very useful in arranging systematically various data derived from observa-

tion, using formulas of the Rydberg-Ritz type which had been developed independently of any theory, and prior to the introduction of quantum theory. This scheme has been modified and altered from time to time to recognize other relationships between spectral lines derived from observation. In its present form it is known as "wave mechanics."

To include x-ray lines in this scheme Bohr attributed them to atoms which had lost one electron only, but not an "outer" one, which would enable the atom to be excited in such a manner as to emit a spectrum of the second order; but an electron from an "inner shell," replacement of which by an electron from a shell farther out, was supposed to result in the emission of an x-ray line. This scheme does not make it possible to calculate any x-ray lines from other lines, at least not with any precision; but it did provide a guide by which classification of observed x-ray lines could be made.

The scheme thus briefly outlined does not account for the absence of the expected lines mathematically anticipated by Bohr's original formula. This is especially difficult to account for in the cases of the elements of small atomic number. The primary system of hydrogen is very fully developed, particularly in solar and stellar spectra, over thirty Balmer lines being reported in the spectra of some stars. In the January number of the *Astrophysical Journal*, S. A. Mitchell reports 35 lines of the Balmer series and lines from H 11 to H 40 of the Paschen series in the flash spectrum of the sun taken during eclipse. The regular spectrum of helium also contains many lines which have been observed, and we have been able to produce many of these lines of hydrogen and helium in the laboratory; but neither in the laboratory nor in the stars have any lines corresponding to the Balmer or Paschen or other series of hydrogen been observed, attributable to other elements, except a very few lines of the Lyman series of lithium, beryllium and boron — too few to make the classification certain.

According to the scheme I am presenting, the regular spectra anticipated by the Rydberg formula (subject to correction based upon observations) would be found if it were possible to exclude from the excitation chamber all sub-elements except the one to which that regular spectrum must be ascribed. This is not possible in the laboratory because the x-ray target is composed of sub-elements of different atomic numbers. The radiation that would be produced by line molecules of one sub-atom only in the *a* configuration is modified by molecules of other sub-atoms of different atomic numbers.

This is not merely an idle scheme, for it can be tested, but only where x-ray lines are observed in sufficiently large numbers. To obtain the necessary data for such test I have used the tables of the last edition of Siegbahn's great work, German edition of 1931. The numerous *K* lines of elements of small atomic number are not given in any English publication of which I know and the earlier edition of Siegbahn which has been translated into English, does not contain them.

Lines corresponding to the Lyman lines of hydrogen are given approximately by the formula

$$\nu = N^2 R \left(1 - \frac{1}{n^2} \right)$$

in which ν is the wave number, N the atomic number and R the Rydberg number. The Rydberg number, as determined from the analysis of spectra, is not an absolute constant. To have a uniform scale for reference, the "theoretical" Rydberg number, calculated by Bohr's formula, is commonly used. All the frequencies recorded by Siegbahn, which will be used in this discussion and in my tables of x-ray levels, are numerically expressed not in wave numbers, but in multiples of the theoretical Rydberg number.

The application of this scheme can readily be explained by an example. The atomic number of sodium is 11. The series limit of the regular spectrum to be expected is about $11^2 R$ and the first two lines corresponding to the Lyman lines of hydrogen are $90.75 R$ and $107.55 R$ respectively, these figures being approximations, for we do not know the exact law by which the values of R increase, and do not accept without experimental or observational confirmation Bohr's assumption that the variation in R is due to increase in mass only.

The nine observed K lines of sodium are given in terms of R at the heads of columns in Table 70 (p. 190). These lines are believed to be derived from the expected lines by deductions of Lyman lines of other sub-elements. If these deductions are added to the observed lines the correct values of the lines attributable to sub 11 may be found. We know from Chapters 5 and 6 that sodium contains sub 1, sub 2 and sub 3, but have no evidence that it contains any sub-element of higher atomic number. Therefore the increments should be found among the Lyman lines of these three sub-elements. As there are nine lines to be accounted for and the increments from which selection must be made are limited in number, it is possible to evaluate the sought-for lines of sub 11 which are found to be $91.19 R$ and $108.07 R$, both slightly greater than anticipated by Bohr's formula. Since there are K lines of other elements to be accounted for, the conditions to be met are more severe than expressed in the foregoing outline. If, instead of finding the Lyman lines of sub 11, we wish to account for the observed lines, we read the table from the bottom upward, successive deductions from the two Lyman lines of sub 11 being made by absorption and re-emission of line molecules of sub-atoms of sub 3, and sub 2 and sub 1.

In Table 70 will be found analyses of the 16 lines of the elements from atomic number 11 (sodium) to atomic number 26 (iron), except argon, for which data are not available.

For convenient reference the theoretical series limit and the lines corresponding to the Lyman, Balmer, Paschen and two other series of hydrogen for the first six sub-atoms in order of increasing atomic number are given in terms of R in Table 68 (p. 188).

For a preliminary review of the data, all the K lines recorded for elements from 11 Na to 21 Sc, with differences from line to line, are given in Table 69. Upon comparison of the difference numbers with those of Table 68, it is seen

that certain ones are common to both tables, and occur repeatedly in Table 69. Thus the number 0.44, which is the difference between two Lyman lines of sub-element 3 in Table 68, occurs as a difference in Al and Na. A critical comparison of all of the difference numbers in Table 69 reveals the fact that every one of them is either a simple difference found in Table 68 or a compound of two or more such differences.

At the time that I discovered this relationship the restriction that all the increments must be Lyman lines and not lines of some other series was arbitrary. The differences used are the same, no matter which series is used to compute them. I no longer regard the restriction as arbitrary in view of the facts discussed in other chapters of this book. It is significant that this restriction leads to values of the first two Lyman lines of the various sub-elements which progress in a regular manner — not, indeed, in the manner assumed by quantum theory, upon which the theoretical Rydberg number was based, but increasing in frequency somewhat more rapidly than that theory calls for. The analogy with the primary spectrum of hydrogen and the corresponding spectrum of helium remains unaltered.

If the hypothesis here presented is worthy of further consideration, it must be consistent not only for each chemical element considered by itself, but from element to element, the peculiarities being accounted for. Table 70 will stand critical study as to detail, although naturally some corrections may be necessary. The regularity of the progressions, however, is shown in Table 71, where first and second differences between the Lyman lines, from element to element, are given. Absolute regularity should not be expected, for all differences are discrete.

We now turn our attention to the *L* lines of x-ray spectra. The record begins with 23 V, for which only one line is recorded. Table 72 gives an analysis for the *L* lines from 23 V to 30 Zn, inclusive. The lines become more numerous as we proceed to elements of higher atomic number, and data are available to extend our Table 72 very considerably, but I have carried it only far enough to show the connection between *K* and *L* systems, involving different elements. The reader is invited to compare Table 70 with Table 72 and to note that the numbers 91.19 and 108.59 found for sodium are found to be origins of *L* lines in 28 Ni, 29 Cu, and 30 Zn, which means that at least some atoms of each of these three elements, Ni, Cu, and Zn must contain at least one sub-atom 11, the heaviest sub-atom of Na.

Table 72 calls for the following sub-elements in at least some atoms of the chemical elements listed.

23 V	Sub-elements 8 and 2
24 Cr	" 9, 3, and 2
25 Mn	" 9 and 2
26 Fe	" 10, 9, 3, and 2
27 Co	" 10, 3, and 2
28 Ni	" 11, 10, 3, and 2
29 Cu	" 12, 11, 3, and 2
30 Zn	" 13, 12, 4, 3, and 2

The table, however, does not inform us whether all of these sub-elements must be present in every atom, or how many of each may be required; nor does it tell us that no other sub-elements may enter into the atomic structure. Combining the information furnished by Tables 70 and 72, we find that if only one of the sub-atoms the presence of which is indicated by x-ray spectra were contained in every atom of a given chemical element the required atomic weights would in some instances exceed the atomic weight ascertained by positive ray analysis and in other instances would be less, as indicated in the following schedule:

	<i>Sub-atoms required</i>		<i>At. weight</i>	<i>Difference</i>
23 V	23 + 8 + 5 + 4 + 3 + 2	= 45	50.96	+ 6
24 Cr	24 + 9 + 5 + 4 + 3 + 2	= 47	52.01	+ 5
25 Mn	25 + 9 + 5 + 4 + 3 + 2	= 48	54.93	+ 7
26 Fe	26 + 10 + 9 + 5 + 4 + 3 + 2 = 59		55.84	- 3 or - 4

In the case of Fe it is obvious that if both 9 and 10 are in the same atom, all the other kinds of sub-elements cannot be present also in that particular atom; and it is also obvious that if only one of these two, 9 and 10, is present in an atom, more than one of smaller atomic number must be present in order to make up the mass revealed by positive ray analysis. Spectra do not reveal the actual structure of individual atoms, but only the sub-elements present in a large number of atoms, more or less separated from the chemical atoms by excitation. Isotopes indicate that in some cases atoms of like chemical properties differ in mass. They do not reveal the structure or indicate that all atoms of like mass are alike in composition. The isotopes of Fe have mass numbers 54 and 56. Mere substitution of sub-atom 9 for sub-atom 10 would not account for this difference but would only change the mass number by one unit. There must be other differences even in the case of these isotopes, and there is nothing to warrant that several different structures of substantially the same mass may not produce chemical atoms of the same chemical properties, undistinguishable by chemical means at present known, but not necessarily unknowable when science has advanced sufficiently, both experimentally and by analysis.

Atoms may be isotopic not only because they are of different composite structure so far as the sub-atoms in their structure are concerned, but also because the sub-atoms themselves may be isotopic. Sub-atomic nuclear structure, in so far as it is revealed by spectroscopy, will be discussed in Chapter 15.

Chapter 8

A Preliminary Model of a Hydrogen Atom

A mechanical or even a pseudo-mechanical model is very helpful, if not necessary, for the initial presentation of any scheme which seeks ultimately to be of practical use in the control of phenomena, even if, after the scheme is more fully developed, the preliminary model is found incomplete or inadequate. For this reason, even in the preliminary discussion of the relationships of observed spectra from different sources, I have used a preliminary pseudo-physical model to account for "levels" as though they were physical properties of atoms or molecules. Perhaps no apology is needed for this. At any rate it is precisely what Bohr did when he first presented his mathematical theory to account for the lines of the primary spectrum of hydrogen. His basic assumption was, and is, that single atoms of hydrogen, unassisted by other atoms or molecules, actually do emit monochromatic quanta of radiation of the frequencies of the primary spectrum.

I have found this assumption inconsistent with the fact that primary levels contribute to the secondary spectrum as well as to the primary, and am convinced that all the spectral lines of hydrogen originate in radiations involving the behavior of more than one electron. The most important part of the characteristic spectrum of hydrogen requiring explanation is the continuous spectrum which invariably accompanies spectral lines. I therefore begin with an atomic model capable of accounting for a continuous spectrum with the characteristic qualities of the characteristic spectrum of hydrogen, but simpler, in order to make mathematical treatment easier at the outset.

The characteristic continuous spectrum of hydrogen does not extend indefinitely into the region of high frequencies. Probably it is of composite origin. When secondary lines are present it extends to wave number 117754.43. Probably when only primary lines are present it does not extend beyond 109678. It is not of uniform intensity, but in general is strong in the Schumann region and falls off in the visible region, and the intensity in any region varies with gas pressure and other conditions of excitation. To make the preliminary model as simple as possible, I will assume that the atom has but one high frequency limit for its characteristic spectrum, and I place that limit at the Rydberg frequency. In a subsequent chapter it will be necessary to modify this model to account for two possible limits instead of one.

For present purposes it will be assumed that a negative electron possesses the mass and the charge assigned to the "slow moving" electron by bal-

listic investigations such as those of Thomson, the interpretation of which is based on the "classical" electromagnetic theory, with the assumption not implicit in that theory that mass and charge may not be affected by velocity with respect to the surrounding medium. I will assume that the structure of the atomic ion is such that the negative electron may be poised with respect to the ionic center at a fixed distance therefrom in any direction, and that it may oscillate radially about that position of poise with a frequency which will have an upper limit as the electron approaches rest but will diminish as the amplitude increases. Such oscillation would occur if the electron were initially displaced from the position of poise and permitted to return. The frequency would gradually increase, and the resulting spectrum would be continuous, with a fixed high frequency limit, at which the energy of radiation would become negligible.

The final or limiting frequency in such a case is given by the equation of ordinary mechanics:

$$\frac{dF}{ds} = 4\pi^2\nu^2m \quad (1)$$

in which F is the force of restitution, s the displacement from the position of poise, m the mass of the electron, and ν the frequency.

The mass of the ion with respect to which the electron is poised will be indicated by M , and we shall assume that M is so many times greater than m so as to allow us to ignore its displacement when the electron oscillates. This will simplify formulas, but a correction may be made later if desirable. The charge of the electron will be assumed to behave as if it were a point charge toward charges at a distance, such as we shall now consider. We do not assume that it is a point charge or a surface charge but leave the matter of its distribution at this stage of our investigation to future inquiry.

When the electron is at a very great distance from the ion, we shall assume that there is attraction between the two according to the inverse square law, that is:

$$F = \frac{e^2}{r^2} \quad (2)$$

But at the distance r_0 between centers the force is zero, since we have assumed poise there. Let us allow for this by assuming that the charge of the ion is not all concentrated at the center of figure, as assumed by Rutherford and Bohr, but is distributed in the space surrounding the center of mass in a manner that is to be ascertained by inquiry. I have tried several formulas in the endeavor to find one that will give results corresponding to what is actually found in the hydrogen spectrum; the best of these is

$$F = \frac{e^2}{r^2} - \frac{e^2 r_0}{r^3} \quad (3)$$

In this equation attraction is indicated by the positive sign and repulsion by the negative sign. The force will be attraction if r is greater than r_0 and

repulsion if it is less than r_0 . The relationship between F and r is graphically indicated in Figure 1.

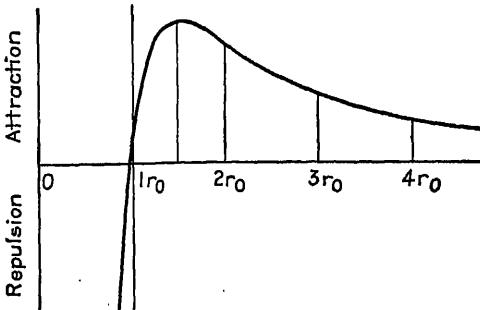


FIGURE 1

Differentiating equation (3) and combining it with (1), we have:

$$\frac{dF}{dr} = \frac{3e^2r_0}{r^4} - \frac{2e^2}{r_0^3} \quad (4a)$$

$$\frac{e^2}{r_0^3} = 4\pi^2\nu^2m \quad \text{when} \quad r = r_0; \text{ hence} \quad (4b)$$

$$\nu^2 = \frac{e^2}{4\pi^2mr_0^3} \quad r_0^3 = \frac{e^2}{4\pi^2\nu^2m} \quad (4c)$$

If we identify ν with the Rydberg frequency, we may obtain a relationship between the dimension r_0 in our ideal atom and Planck's constant. The Rydberg frequency is known to be

$$\nu = \frac{2\pi^2e^4m}{h^3} \quad (5)$$

This is Bohr's formula, which is known to be empirically correct and may be used without acceptance or denial of any of the assumptions which he found convenient to use in deriving it. By combining equations (4) and (5) we obtain

$$h^3 = \sqrt[3]{2\pi^2e^4mr_0} \quad \text{or} \quad r_0 = h^3 \div \sqrt[3]{2} \times 2\pi^2e^4m \quad (6)$$

This interpretation makes Planck's constant an attribute of matter, due to the structure of the atomic ion and of the electron, and not a property of radiation *per se*. In this concept we follow the philosophy of Planck. But thus far we have applied the concept to only one particular theoretical atom. To be valid it must be capable of application to all chemical matter.

The energy required to dissociate this ideal atom is found by integration, thus:

$$dW = Fdr = \left(\frac{e^2}{r^2} - \frac{2e^2r_0}{r^3} \right) dr \quad (7)$$

$$W = \int_{r_0}^{\infty} Fdr = e^2 \int_{r_0}^{\infty} \left(\frac{1}{r^2} - \frac{r_0}{r^3} \right) dr = e^2 \left(\frac{r_0}{2r_0^2} - \frac{1}{r_0} \right) = \frac{e^2}{2r_0}$$

or, substituting the value of r_0 in terms of h ,

$$W = \sqrt[3]{2} \times \frac{\pi^2e^4m}{h^3}$$

This is not the energy required to dissociate Bohr's atom, which he computes to be

$$W = \frac{2\pi^2 e^4 m}{h^2}$$

Although his formula for the Rydberg number is correct, as can readily be ascertained by applying it to the observed Rydberg limit, his formulas for energy are not verified by any direct observations but rest entirely upon assumptions. I have pointed out that my model does not lead to the same results as his in this matter in order that there may be no misapprehension in the mind of the reader on so important a matter as the presentation progresses.

If the electron is not removed from the ion completely but merely displaced to some distance $r_x > r_0$ and there brought to momentary poise, the energy required for such displacement will be:

$$W = \frac{e^2}{2r_0} - \frac{e^2}{r_x} + \frac{e^2 r_0}{2r^2 x}, \quad \text{or if} \quad r_x = r_0 x \quad (8a)$$

$$W_x = \frac{e^2}{2r_0} \left(1 - \frac{2}{x} + \frac{1}{x^2}\right) = \frac{e^2}{2r_0} \left(1 - \frac{1}{x}\right)^2 \quad (8b)$$

If, on the other hand, the electron be pressed into the ion to the distance r_y from the center, the energy required to do this will be

$$W_y = \frac{e^2}{2r_0} \left(\frac{1}{y} - 1\right)^2 \quad (8c)$$

If the electron is oscillating, were the radiation during one oscillation negligible (as it must be very small indeed), $W_x = W_y$. Then

$$\frac{1}{x} + \frac{1}{y} = 2 \quad (9)$$

In this expression x may have any value greater than 1 and y any value between 1 and 0.5.

To ascertain the frequency of oscillation for any amplitude, we must consider the time required for the electron to move from any position defined by r_y to the corresponding position r_x .

$$\alpha = \frac{F}{m} = \frac{e^2}{m} \left(\frac{r_0}{r^3} - \frac{1}{r^2}\right) \quad (10a)$$

is the acceleration at any distance r . There will be repulsion if r is less than r_0 and attraction if r is greater than r_0 . Consequently, acceleration will always be in the direction toward the position of poise, and the velocity of the oscillating electron will be greatest when passing that position. For convenience we assume that the electron is initially at momentary rest at r_y and consider repulsion the positive force accelerating it outwardly. From the position of momentary rest to that of maximum velocity, the time required can be computed. We have

$$v = \frac{dr}{dt} \quad \alpha = \frac{dv}{dt} = \frac{d^2r}{dt^2} = \frac{e^2(r_0 - \frac{1}{r^2})}{m} \quad (10b)$$

Multiplying both sides of this equation by the equality $\frac{2dr}{dt} dt = 2dr$ and integrating, we have

$$\left(\frac{dr}{dt}\right)^2 = \frac{2e^2}{m} \left(\frac{1}{r} - \frac{r_0}{2r}\right) + C = v^2 \quad (10c)$$

From these expressions, by strictly mathematical steps in which I have had the assistance of a friend familiar with advanced methods of calculus, it may be shown that

$$v = \frac{e}{2\pi\sqrt{mr_0^{\frac{3}{2}}}} \times \frac{(2y - 1)^{\frac{1}{2}}}{y^3} \quad (11a)$$

$$\Delta = \frac{2y^2 r_0}{2y - 1} \quad (11b)$$

$$\frac{v}{\Delta} = \frac{e}{4\pi\sqrt{mr_0^{\frac{3}{2}}}} \times \frac{(2y - 1)^{\frac{1}{2}}}{y^5} \quad (11c)$$

in which Δ is total amplitude of oscillation. In these equations y is the only independent variable. A plot of the ratio $\frac{v}{\Delta}$ given in Figure 2 shows graphically the relationship between maximum frequency (the Rydberg frequency in this case) and amplitude of oscillation. When the amplitude

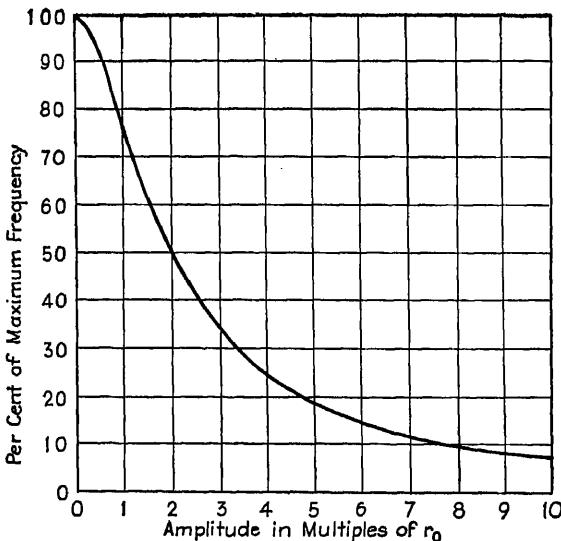


FIGURE 2

is 0, $y = 1$ and the frequency is maximum. If the amplitude should become infinite, the frequency would be 0, and y must be 0.5; but if y is less than 0.5, the electron will be expelled to an infinite distance and will still have some residual velocity.

If in this system there is any oscillation of the electron, there must be loss of energy by radiation. If no energy is supplied from some other source, the amplitude of oscillation must diminish and the frequency increase until

the Rydberg frequency is attained, by which time the radiation lost per oscillation and the residual energy of oscillation would be negligible. The radiation would leave the system in all directions, distributed in accordance with well known laws, and not as "quanta" or slugs, and it would travel with the velocity of light in the surrounding medium. The total quantity of energy to be distributed in this way would depend entirely upon the initial displacement of the oscillating electron. The intensity of each pulse at some appreciable distance from the source in the same direction would vary according to the inverse square law. Consequently, the amount that could arrive at a distant atom or molecule would be very minute, and one such pulse alone or a succession of pulses derived from a single oscillating electron would not at best be able to do more than very slightly push the distant electron in a given direction. It could not possibly cause a disturbance in the distant electron at all comparable with the disturbance at the source.

If the amplitude of the original displacement is known, the total energy to be radiated also can be known, and for any given amplitude the energy radiated per pulse is calculable. If Q represents charge, α acceleration, and c the velocity of light, the rate at which energy is radiated is given by the equation

$$\frac{dW}{dt} = \frac{2Q^2\alpha^2}{3c^3} \quad (12a)$$

which becomes, in the system under discussion,

$$\frac{dW}{dt} = \frac{2e^2\alpha^2}{3c^3} = \frac{2e^4}{3c^3r_0^4} \left(\frac{1}{y^3} - \frac{1}{y^5} \right)^2 \quad \text{or} \quad \frac{2e^4}{3c^3r_0^4} \left(\frac{1}{x^3} - \frac{1}{x^5} \right)^2 \quad (12b)$$

The wave chain consists of a series of pulses in one direction alternating with pulses of less intensity in the opposite direction. The effect upon a free electron at a distance from the source would be to accelerate it in one direction — to impart to it a calculable velocity. If the electron encountered is "bound" in an atom or molecule, the effect of the pulses may be cumulative or it may be random, depending upon the nature of the binding and the frequency with which the pulses arrive.

From the premises already set forth, equations may be derived which will give the length of time required for an electron to pass from any given distance from the nuclear center less than r_0 , at which it may be momentarily at rest, to any greater distance within the range through which it may oscillate; also the velocity at any instant after momentary poise. It is found that the more deeply the electron penetrates, the shorter the period of time that it is closer to the center of the ion than the distance r_0 and consequently the shorter as well as the more intense the pulse of radiation due to repulsion, while the time that the electron is farther out than r_0 is increased, but the intensity of the pulse due to attraction is lessened. When the amplitude of oscillation is very small, the motion is very nearly simple harmonic at almost the Rydberg frequency, but the intensity is very feeble;

but when the amplitude is large, the radiation approaches a series of sharp intense pulses in one direction separated by relatively long intervals of time.

For graphic illustration I have calculated the necessary quantities to plot three graphs (Figure 3), the upper one illustrating the relationship between

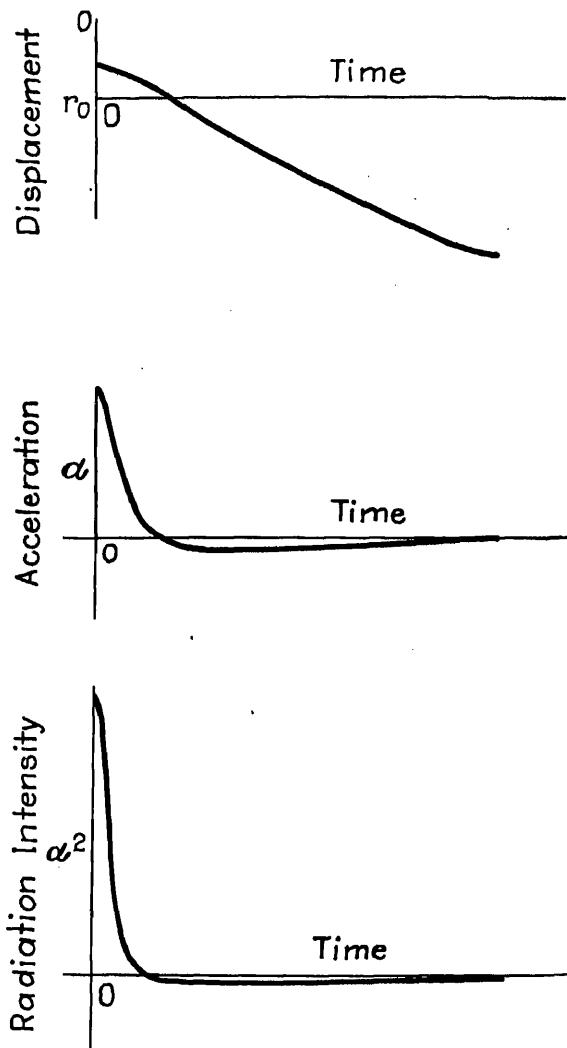


FIGURE 3

deflection and time, the middle one the relation between acceleration and time, and the lower one the relation between intensity of radiation and time, for a period of half a wave length, when the closest approach of the electron to the center of the ion is $0.6r_0$.

The analysis thus far shows that without violence to electromagnetic theory the proposed model illustrates how an atom might give rise to a

series of waves that, if sufficiently plentiful, might produce a record of a continuous spectrum with a definite upper frequency limit, such as that of hydrogen. It does not indicate how monochromatic radiation could be produced, but, quite to the contrary, it indicates that no lines could be expected from such atoms acting individually. The production of a line would require cooperative mechanism of some kind, the possibility of which must be investigated.

Chapter 9

The Possibility of Producing a Spectral Line

We will consider briefly the possibility of producing monochromatic radiation by the cooperation of several atoms of the general character outlined in Chapter 8, which alone could emit only continuous spectra with a fixed high frequency limit. Observed lines are not strictly monochromatic, even under the most favorable circumstances. Lines of the Balmer series of hydrogen may be very sharp when the gas pressure is very low and the excitation feeble, but they broaden as the gas pressure is increased, and may even become so broad that they merge. It is not unreasonable to think that they may be derived by the cooperation of sources which are not of themselves even approximately monochromatic, by some process of stabilization.

The phenomena of interference suggest that the lines are due to wave trains and that these trains must be at least approximately monochromatic for very many waves in sequence. Such wave trains might originate within one source, by a process of stabilization due to structure, or as difference frequencies between trains which are not of themselves monochromatic, but interact at their sources in a manner which stabilizes the difference frequency.

In all the chapters discussing classification of lines, I have followed the usual practice of considering lines as differences between levels, and have analyzed the levels as though they were real states of a physical kind rather than merely mathematical conveniences which enable us to make practical use of series formulas. However, in proceeding to assign sources for the radiation, it is necessary for us to bear in mind that lines are what we observe and measure, not levels, except in the exceptional cases where the levels coincide with limits of characteristic continuous spectra, such as the level 117754.43 of hydrogen. For instance, the wave numbers of the Balmer level, the Paschen level, and all the other levels of the primary spectrum of hydrogen may be most advantageously derived as differences between the wave numbers of Lyman lines, as readily as by series formulas based upon mathematical considerations of another kind, involving hypotheses which are not directly verifiable by observation. Similarly, all the lines of all other series of the primary spectrum may be derived as differences between Lyman lines. There may be small discrepancies to be accounted for, which have a bearing upon the determination of the original sources — a matter to be determined by most careful consideration of all

available data rather than assumed by accepting some *a priori* hypothetical scheme.

In attempting to get some insight into the possible process of stabilization of frequencies, I will first discuss very briefly what would be expected as the frequency of an electron oscillating radially between two such idealized hydrogen atoms as discussed in Chapter 8. In this case it is necessary to consider the force exerted by the ions upon one another, as well as the forces between the ions and the electron between them. To make this case as simple as possible, we will assume that the electron has no component of motion except along the line joining the centers of the ions, the oscillation being in the same straight line. In a later chapter it will be necessary to consider the motions that would occur if more than one electron were involved in the system. Therefore it will save time to enunciate now the laws which govern the forces between the respective particles.

As given in the preceding chapter, the force between the electron and one ion is

$$F_1 = \frac{e^2}{r_x^2} - \frac{e^2 r_0}{r_x^3} = \frac{e^2}{r_0^2} \left(\frac{1}{x^2} - \frac{1}{x^3} \right) \text{ where } x = \frac{r_x}{r_0}$$

$$F_2 = \frac{e^2}{r_x^2} = \frac{e^2}{r_0^2} \times \frac{1}{x^2}$$

is the force between two electrons at all distances which we shall consider. It always is repulsion.

$$F_3 = \frac{\left[e \left(1 - \frac{2r_0}{rx} \right) \right]^2}{r_x^2} = \frac{e^2 (x - 2)^2}{r_0^2 x^4}$$

is the force of repulsion between two theoretical ions, at all distances which we shall consider in this chapter.

These formulas are mutually consistent. The first and last can be accounted for as due to distributed charge about the ionic center. We will, however, make a new assumption, which is that these forces are unmodified by the presence of particles between or in the neighborhood of the particles under consideration, throughout the range of distances which is considered in this preliminary investigation. Only by assuming this can the treatment be rendered strictly and critically mathematical at this time.

When the number x is large, all these formulas approximate the inverse square law.

For convenience of comparison of how these forces are related to one another at corresponding distances, I have plotted graphs in Figure 4, from which it is seen at a glance that the force between an electron and an ion is zero when their centers are the distance r_0 apart, and that between two ions zero when the centers are $2r_0$ apart. Thus an electron between two ions which are at the critical distance apart, at which they neither attract nor repel one another, would itself be neither attracted nor repelled by either ion, if once brought to rest in the position midway between them. Without

the electron, the ions could be poised with respect to one another; but the poise would be unstable, for if there were the slightest displacement either inward or outward, repulsion, not attraction, would result.

The two ions with the single electron between them represent the molecular ion of mass 2 and charge $+e$. Positive ions of such mass and charge are

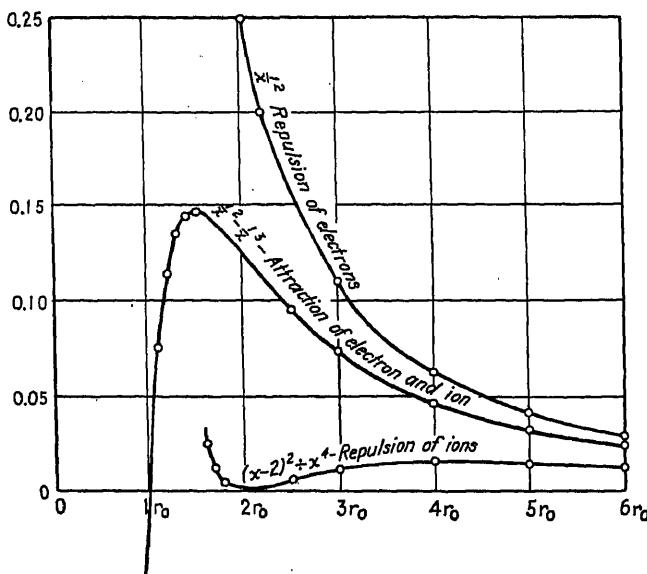


FIGURE 4

found by positive ray analysis. If they are represented approximately by our preliminary model, when the ions are pressed closer together and begin to repel one another, the electron does not remain between them on the line joining their centers but moves away from that center line, maintaining its distance of poise from the center of each ion. But when the ions are moved farther apart than the poised position and the electron is not set into oscillation, it poises itself half way between their centers, provided their distance apart is not too great, the critical distance being $3r_0$.

If the amplitude of oscillation of the electron is not too great, it would be capable of oscillating between the ions along the line joining their centers, if once set in motion. Other types of motion are, of course, possible, but this kind is the simplest to consider. In such a case the distance between the ions could vary, and the amplitude of the oscillation of the electron also could vary. Both of these variations would affect the frequency of the oscillation and consequently that of the radiation emitted by it.

Without exact mathematical analysis, it is obvious that if the ions were moving apart and the amplitude of the oscillations was constant, the frequency would diminish; while in the preceding chapter it has been shown that if the amplitude diminishes when only one ion is present, the frequency

will increase. It is thus evident that in the ion we are considering there will be two factors affecting the frequency simultaneously, if the ions are approaching one another, and the amplitude of the electron's oscillation is diminishing as a result of loss of radiation energy by radiation; one of these factors tends to increase the frequency of oscillation and the other to diminish it. The result of the balancing of these opposite tendencies, owing to the rate at which radiation occurs, will have a tendency to stabilize the frequency as the position of final quiescent poise is approached. Reversing this process, if the amplitude of oscillation of the electron were increasing owing to absorption of energy from without the system, and at the same time the ions were moving apart, the resonance frequency of absorption would be stabilized. The degree to which such stabilization could take place and the range of amplitudes through which approximately monochromatic radiation could occur is not at present considered.

It is necessary here, however, to point out that in this preliminary model oscillation of the electron with any moderate amplitude will affect the distance apart at which the ions may be poised, in case the amplitude of oscillation were constant. This must follow from the fact that in this model the force of repulsion of the electron for an ion increases more rapidly as the distance between the electronic and ionic centers decreases to less than r_0 than the force of attraction increases as the distance between centers increases beyond r_0 .

In the chapter to follow it will be necessary to apply the equations set up in this chapter to the problem of two complete atoms, that is, of two positive atomic ions and two electrons, which will lead to a preliminary interpretation of the origin of the first Lyman line of hydrogen. This model, however, will require modification before it can account for the many lined spectrum and for fine structure and other peculiarities in the primary spectrum itself. Therefore it would not be profitable to continue this analysis of the possibilities of the molecular ion, as the purpose of this preliminary treatment is to show, in the simplest manner, that the production of approximately monochromatic radiation is not an impossibility in a system which is consistent with usually recognized electromagnetic laws.

Chapter 10

The First Lyman Line of Hydrogen

In Chapter 2 the classifications of the lines of both primary and secondary spectra show conclusively that every line may be accounted for numerically either as a simple arithmetical difference between the wave numbers of pairs of levels, or as a result of the compounding of two or more such simple differences. The goal of classification, with me as well as with others, was evaluating the levels precisely and classifying them systematically in the simplest possible manner. The classification itself is not governed by theory as to the process by which the line is emitted, or even by the nature of the bodies in which the radiation originates.

But during this classification work I did entertain the idea that these levels represented physical realities and were not merely mathematical conveniences. I did not think them states of atoms, but rather properties of molecules of certain ascertainable configurations, one level to each variety of molecule, the lines resulting from cooperation of differently constituted molecules that happened to be close enough together to stabilize a frequency difference. I supposed that if the proper approach to the problem could be found, it might be possible to trace the Lyman level to one body (as I seem to have done in the case of the ideal atom) and the Balmer level to a combination of two atoms, the line resulting from the difference of frequencies emanated by these two bodies, although the frequency of neither was constant.

The nomenclature which I used in my classification tables was in keeping with this idea, which I have since found requires modification but not complete abandonment. This in no way affects the classification, which demonstrates that "combinations" do take place between the primary levels and other levels in the development of the many lined spectrum and much else of importance besides.

A large part of the information in Chapter 2 of this book was published in 1942. Part of the material in this chapter was published in a pamphlet of later date. The investigation led to the result that the Balmer level is itself a "combination," possibly little more than a mathematical convenience in classification. This came as a surprise to me and was the direct result of computation, not anticipated by speculation. Those computations were very laborious and required a great deal of time. I present a summary of them in as brief form as possible.

In general, there are three possible arrangements in which two simplified

atoms such as have been under discussion could be in combination with the four particles poised with respect to one another. In only one of these could the centers be arranged in the same straight line, electrons and ions alternating. In the other two the particles would all be in the same plane, their centers at the four corners of a rhombus, as indicated in Figure 5, in which the dots represent the centers of the ions and the small circles the

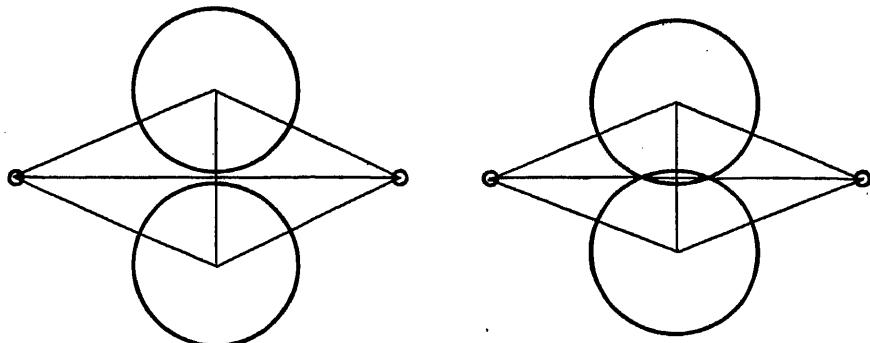


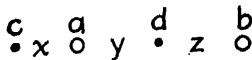
FIGURE 5

electrons. The radius of the larger circles represents the distance r_0 from the center of the ion at which the electron could be poised if the other atom were not present. There would be attractions along the sides of the rhombus and repulsions along the diagonals. Of these two arrangements, that shown on the right-hand side would not be stable. If subjected to the slightest shock, it would transform itself into the form shown on the left, because the electrons repel one another at all distances that come into consideration, and there is one distance apart at which the ions do not repel one another. For our ideal mathematical atom it is not difficult to compute the stable configuration for these molecules from the formulas for forces already given. It would be more difficult to compute the limiting frequencies; this is not worth while, for the final result could not be verified by reference to the spectrum of hydrogen itself. This is because our preliminary model is incomplete, accounting for only one limit of the characteristic spectra of hydrogen instead of two; and although this defect, as will be shown, does not render the atomic model useless in tracing the origins of the primary spectral lines, it does impair its applicability to the secondary spectral lines very decidedly — a defect which will have to be remedied later.

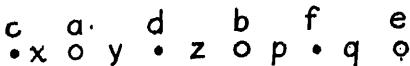
Furthermore, it is known from the work of Bonhoeffer and others that instead of there being one stable form of the normal hydrogen molecule, there are two, both of which are present in the gas at ordinary temperatures and pressures, although they may be caused to vary in relative abundance by changes in temperature and other physical conditions. Our ideal model would permit only one.

We now direct our attention to the configuration of the two-atom molecule in which the centers of the particles lie in a straight line. This is repre-

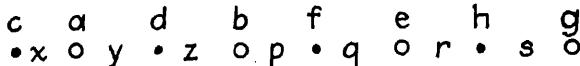
sented diagrammatically in Figure 6. The centers of the heavy particles are indicated by dots and the negative electrons by circles. For convenience in reference to the figure in connection with formulas, the positive ions are designated by c and d and the electrons by a and b , this having been the arrangement which I happened to use when I first began this investigation



2 Atoms in line



3 Atoms in line



4 Atoms in line

FIGURE 6

some years ago, which I have followed since for the sake of avoiding confusion. I have always placed the terminal electron at the right-hand end of the line and the terminal ion at the left. The distances between adjacent particles, center to center, from left to right, are designated by x , y , and z or by r_0x , r_0y , and r_0z , as may be most convenient. The resultant force exerted by the combined attractions and repulsions of the three other particles on any one particle is designated by F_a , F_b , F_c , or F_d . Since the particles are arranged in a straight line, these forces are given by the following equations.

$$F_a = \frac{e^2}{r_0^2} \left\{ \left[\frac{1}{x^2} - \frac{1}{x^3} \right] - \left[\frac{1}{y^2} - \frac{1}{y^3} \right] + \frac{1}{(y+z)^2} \right\} \quad (1a)$$

$$F_b = \frac{e^2}{r_0^2} \left\{ \left[\frac{1}{(x+y+z)^2} - \frac{1}{(x+y+z)^3} \right] + \left[\frac{1}{z^2} - \frac{1}{z^3} \right] - \frac{1}{(y+z)^2} \right\} \quad (1b)$$

$$F_c = \frac{e^2}{r_0^2} \left\{ - \left[\frac{1}{x^2} - \frac{1}{x^3} \right] - \left[\frac{1}{(x+y+z)^2} - \frac{1}{(x+y+z)^3} \right] + \frac{(x+y-2)^2}{(x+y)^4} \right\} \quad (1c)$$

$$F_d = \frac{e^2}{r_0^2} \left\{ \left[\frac{1}{y^2} - \frac{1}{y^3} \right] - \left[\frac{1}{z^2} - \frac{1}{z^3} \right] - \frac{(x+y-2)^2}{(x+y)^4} \right\} \quad (1d)$$

These formulas hold for all spacings of the particles which we shall consider; but there is poise only when all of these forces are zero.

To find the stable configuration I resorted to a process of approximation. Arbitrary values of the three unknowns, x , y , and z , were assumed and the resulting forces computed. The quantity x was then varied until a value of x was found that made F_c zero. Then y was varied until a value was found that made F_a zero. Then z was varied until a value was found that made

F_d zero. Of course by this time none of the forces on any other of the particles a , b , or c was zero; but the same steps were repeated in the same order until all the resultant forces were very nearly zero. The accuracy of the method is limited by the number of approximations one is willing to make and in my case also by the fact that I performed the computations with the use of a calculating machine with no more than eight keys to the row.

Final results are given in the following table.

		F_o	F_a	F_d	F_b
x	.9472079	+ .00212015	- .00212015		
y	1.1935399		- .11383078	+ .11383078	
$x + y$	2.1407478	+ .00094323		- .00094323	
z	1.1904482			- .11288737	+ .11288737
$y + z$	2.3839881		+ .17595104		- .17595104
$x + y + z$	3.3311960	- .06306252			+ .06306352
Total		- .00000014	+ .00000011	+ .00000018	- .00000015

We now are ready to inquire into the limiting frequencies of the electrons a and b . As in our former inquiry, for present purposes we shall regard the ions as so heavy as not to be affected appreciably by the oscillations of the electrons. They may be regarded as fixed. The electrons, however, cannot be regarded as fixed with reference to one another. Owing to this, the problem of the oscillation is far more difficult than in the case where a single electron is oscillating between two ions.

Assuming that the molecule might have been at rest in the final configuration, the rapid approach of another electron might disturb one of the two resident electrons more than the other; or, if the configuration was being formed by the union of two atoms, the initial excitation might be very complex and undoubtedly different in different collisions. It would be only during the final stages of readjustment that anything like order could be established. But it at least is evident that the two electrons would oscillate partly with respect to the fixed ions and partly with respect to one another; and since under the simplest condition, which alone will be considered, they are oscillating in the same straight line and quite close together, in comparison with their distance from any observer, their charges being equal, the radiation reaching the observer would be indistinguishable from that observable if there were only one source. It would be a difference frequency of some kind, whether a variable frequency or a constant frequency depending upon the nature of the individual oscillations of which it was compounded. Thus we are confronted with the problem of computing the frequencies of the electrons individually. Let us attack this by attempting to ascertain the final frequencies, that is, those just before rest is attained. The difference between the individual frequencies at this limit ought to enlighten us somewhat about what to expect when the amplitudes are appreciable, though it will not give us a complete solution of the problem.

Differentiating the equations for F_a and F_b , and remembering that $dy = -dx$, we have

$$\frac{dF_a}{dz} = \frac{e^2}{r_0^3} \left\{ \left[\frac{3}{x^4} - \frac{2}{x^3} \right] + \left[\frac{3}{y^4} - \frac{2}{y^3} \right] + \frac{2}{(y+z)^3} \left(1 - \frac{dx}{dz} \right) \right\} \quad (2a)$$

$$\frac{dF_b}{dz} = \frac{e^2}{r_0^3} \left\{ \left[\frac{3}{(x+y+z)^4} - \frac{2}{(x+y+z)^3} \right] + \left[\frac{3}{z^4} - \frac{2}{z^3} \right] + \frac{2}{(y+z)^3} \left(1 - \frac{dx}{dz} \right) \right\} \quad (2b)$$

In these equations the values of $\frac{dz}{dx}$ are variable, and consequently there is no fixed value of either $1 - \frac{dx}{dz}$ or $1 - \frac{dz}{dx}$. Nevertheless, there may be mean values, and the frequency of radiation of each electron, though slightly variable, may still be almost constant. Consequently we may write, following the same line of reasoning as in the case of the atom,

$$\nu_a^2 = \frac{e^2}{4\pi^2 m r_0^3} \left\{ \left[\frac{3}{x^4} - \frac{2}{x^3} \right] + \left[\frac{3}{y^4} - \frac{2}{y^3} \right] + \frac{2}{(y+z)^3} \left(1 - \frac{dx}{dz} \right) \right\} \quad (3a)$$

$$\nu_b^2 = \frac{e^2}{4\pi^2 m r_0^3} \left\{ \left[\frac{3}{(x+y+z)^4} - \frac{2}{(x+y+z)^3} \right] + \left[\frac{3}{z^4} - \frac{2}{z^3} \right] + \frac{2}{(y+z)^3} \left(1 - \frac{dx}{dz} \right) \right\} \quad (3b)$$

which will give mean values for the final frequencies if mean values of $\frac{dz}{dx}$ can be found.

Substituting the values of x , y , and z for the position of poise for those in the foregoing equations, we arrive at

$$\nu_a^2 = \frac{e^2}{4\pi^2 m r_0^3} \left[1.3734424 + .3020343 + .1461066 \left(1 - \frac{dx}{dz} \right) \right] \quad (4a)$$

$$\nu_b^2 = \frac{e^2}{4\pi^2 m r_0^3} \left[.0297416 + .3082629 + .1461066 \left(1 - \frac{dx}{dz} \right) \right] \quad (4b)$$

If we can find mean values for $\frac{dz}{dx}$ for each of these equations, we can compute mean values for each of the frequencies sought. Since the electrons a and b obviously oscillate at different frequencies, it is obvious that sometimes they are moving in the same direction, sometimes in opposite directions, and sometimes one is momentarily at rest while the other is moving either toward or away from it. Not being able to determine this mean value mathematically from the premises assumed, I have tried to approximate it by trial, beginning with the assumption that the effect of the electrons upon one another as stability is approached is so slight that it may be neglected in a first approximation. This gives

$$\nu_a = \frac{e}{(2\pi m^{\frac{1}{2}} r_0^{\frac{3}{2}})} [1.6754766^{\frac{1}{2}} = 1.2944] \quad (5a)$$

$$\nu_b = \frac{e}{(2\pi m^{\frac{1}{2}} r_0^{\frac{3}{2}})} [.27852135^{\frac{1}{2}} = .5277] \quad (5b)$$

$$\nu_a - \nu_b = \frac{e}{(2\pi m^{\frac{1}{2}} r_0^{\frac{3}{2}})} [.7667] \quad (5ab)$$

The limiting frequency in our ideal atom was found to be $\nu_0 = \frac{e}{2\pi m^{\frac{1}{2}} r_0^{\frac{3}{2}}}$.

Therefore our first approximation to the mean frequency to be expected of the two-atom line molecule is .7667 times the Rydberg frequency.

Electron *b* is farther from the ions than electron *a*. On the average we would expect $\frac{dz}{dx}$ to be greater than 1, in which case $1 - \frac{dz}{dx}$ is negative and $1 - \frac{dx}{dz}$ is positive. Then something should be subtracted from 1.6754766 and something added to .27852136 to obtain mean values of v_a and v_b . By making trials I find that $\frac{dz}{dx} = 1.09$ gives a close approximation, yielding the following result.

$$\begin{array}{ll}
 1 - \frac{dz}{dx} = -.09 & 1 - \frac{dx}{dz} = .0826 \\
 .1461066 \times -.09 = -.013149594 & .14610466 \times .0826 = .01106840 \\
 \underline{1.6754766} & \underline{.27852136} \\
 \hline
 1.662328 & .28958976 \\
 \text{Square root} & .5381 \\
 \text{The difference is} & .7512
 \end{array}$$

This is not finding the mean value of $\frac{dz}{dx}$ by computation based upon physical principles, but it is suggestive of the values of certain quantities in case the first Lyman line actually originated in a molecule of the type described. It would mean that one electron vibrates at a mean frequency 1.2893 times the Rydberg frequency and the other at a mean value .5381 times the Rydberg frequency. The ratio of these is 2.39, which means that on the average, electron *a* makes 2.39 complete oscillations while electron *b* makes one. This irregularity would be in the nature of imposing upon the difference frequency observable, that is, three-fourths of the Rydberg frequency, another sequence of pulses of much less intensity. The only frequency we probably can discover by usual optical methods, including interferometer measurements, would be the mean or average frequency; to detect that we have to use means that reveal not single wave chains originating in single molecules, but the combined results of innumerable such chains, each making but a feeble contribution at a great distance from its source.

If it is conceded that two such theoretical atoms in the configuration suggested would emit radiation if excited, and that the final frequency when the intensity approached zero would be almost the same as that of the first Lyman line, what warrant is there that such frequency would be maintained long enough or at sufficient intensity to contribute monochromatic radiation? From the discussion in Chapter 4 it seems probable that the energy to be radiated must be drawn from the kinetic energy developed by the acceleration of the atoms toward one another in the process of forming the molecule, or its attaining quiescence after excitation derived from electron impact or radiation from some other source.

We shall consider first the attraction between two such atoms, assuming that they approached one another without developing any oscillatory

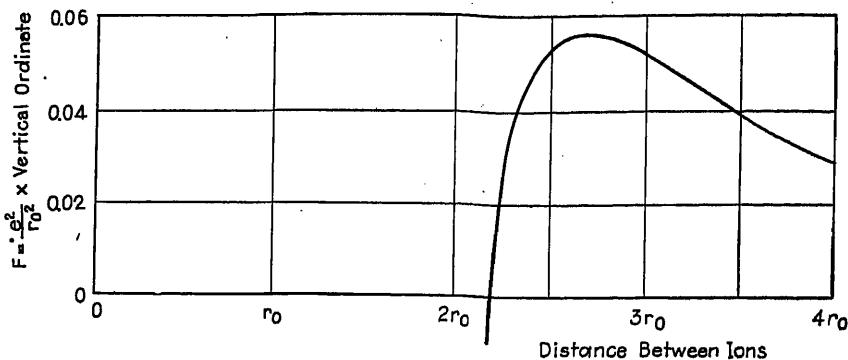


FIGURE 7

motion, or — what amounts to the same thing — that the ions were arbitrarily brought to definite distances apart and held there until their electrons had adjusted themselves in poised positions. I have made such calculations, the results of which are set forth graphically in Figure 7, from which it may be seen that the force would be repulsion if the ions were

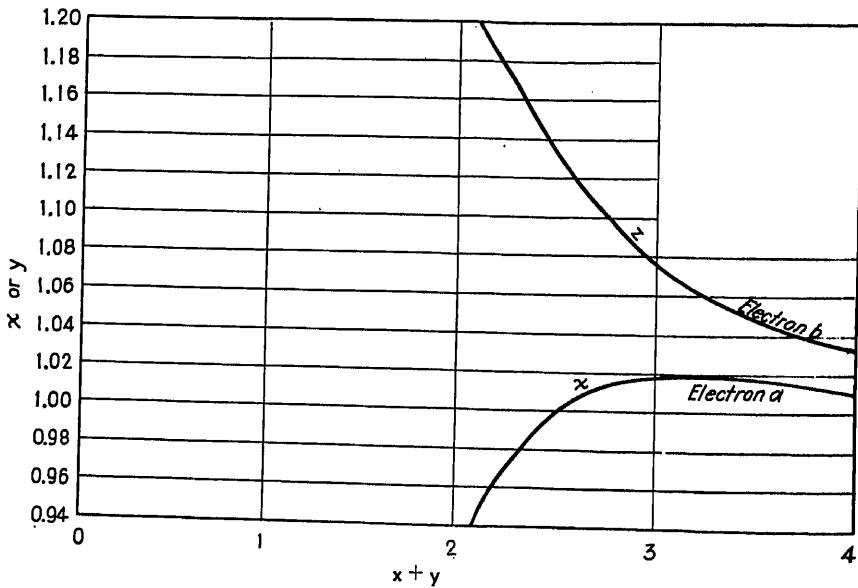


FIGURE 8

closer together than $2.14r_0$ — zero at that distance and attraction at any greater distance, the maximum attraction being at about $2.7r_0$. In Figure 8 the distances of the electrons from their respective ions when the ions are various distances apart are indicated graphically. It shows that the poised

position for electron *a* is increasingly closer to its ion as the atoms approach one another, while electron *b* steadily increases its distance from both ions. Limiting frequencies for each configuration, if the ions were prevented from moving, are calculable, and are compared in Figure 9. Were such conditions natural when the ions were undergoing acceleration, the resulting difference frequency would correspond to a continuous spectrum, with the first Lyman line frequency as its limit, and there would be no monochromatic radiation.

But if the approach of the ions were not arbitrarily restrained, but they were permitted to approach one another freely, they could not reach poised

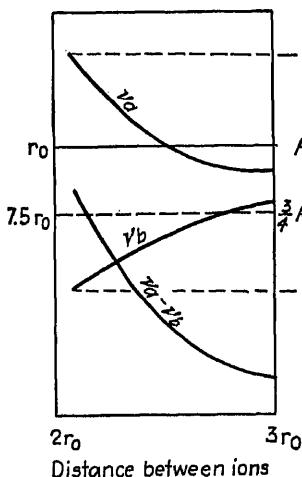


FIGURE 9

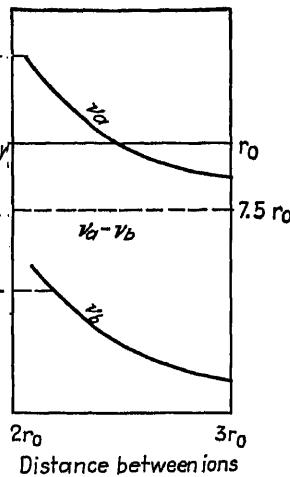


FIGURE 10

positions without setting up oscillations of a very different character from those where the amplitude is vanishingly small. If both atoms were vibration-free when they began their approach, as they acquired velocity toward one another most of the kinetic energy at first would be in the ions, which are more than 1800 times as massive as the electrons. This would carry the ions past the position of poise, and would cause acceleration of electron *b* away from the combination. Thus at least one electron would be violently excited as a result of first collision, and thereafter its frequency would be very much lower than the frequency of electron *a*. The frequency difference would therefore be increased. Radiation would, of course, accompany oscillations of any kind, no matter how complicated, and the internal energy of the system would be diminished until comparative regularity was established in the oscillations of the ions with respect to one another. When, however, the oscillation of the ions about their mean position became feeble, there would be approach to regularity in the oscillations of the electrons, the difference frequency becoming stabilized. The difference frequency would become constant if the rate of increase in frequency of

electron *b* were the same as that of electron *a*, as indicated in Figure 10. Whether in nature such complete stabilization could occur, or whether it could occur with the special mathematical model which I have used thus far in this discussion, presents a mathematical problem which I am not able to solve with precision; but that there would be some stabilization is beyond question. It might be that the stabilization would be sufficient to produce a sharp spectral line only in the very last stages of attaining stability, but that previous to that last stage there would be sufficient stabilization to produce orderly wave chains of varying frequency, which in their turn could "combine" with one another to produce more nearly monochromatic wave chains. The number of complete oscillations produced in this way capable of interfering with one another to produce effects observable by use of an interferometer could be observed, and thus the approximate actual length of monochromatic wave chains or the monochromatic portions of wave chains could be counted.

If the first Lyman line of hydrogen, or wave chains approaching it, is produced by hydrogen atoms combined into two-atom molecules after the manner described, longer line molecules of the same general character might be expected to produce other lines, most likely the lines of the primary spectrum. Although it involved a great deal of work, for the method of investigating by approximations is arduous, I have been able to determine approximate results for line molecules containing three and four atoms in line. These will be discussed in the next chapter. It may be remarked here, however, that the Balmer level seems to be a difference between the frequency limit of the solitary atom and the limiting frequency of a molecule containing two similar atoms in alignment, and not a frequency or a limit characteristic of any one atom or molecule. It is quite possible that the actual process of producing a monochromatic wave train is more involved than indicated in the discussion contained in this chapter, and it will be shown in later chapters, in some instances, that a large number of steps is required to produce sufficiently stabilized frequencies to give rise to the observable spectral lines of the many lined spectrum.

Chapter 11

The Primary Lines of Hydrogen

By methods analogous to those outlined in Chapter 10, but much more lengthy, stable configurations and frequency limits of model line molecules of three, four, or more atoms in line may be found, approximately. I have made the necessary calculations for three and four atoms in the line, with results as follows.

For the three-atom molecule we will assume that another atom has become attached to the right-hand end of the line molecule represented diagrammatically in Figure 6, designating the additional electron by e and the additional ion by f . The distances between successive particles will then be designated by x, y, z, p , and q . For the four-atom molecule the additional electron is identified by g , the ion by h , and the distances between particles by x, y, z, p, q, r , and s . These distances are multiples of the distance r_0 . When all the particles are poised without oscillation, they are as given in the following schedule:

<i>2 Atoms</i>	<i>Difference</i>	<i>3 Atoms</i>	<i>Difference</i>	<i>4 Atoms</i>
x .947207	.011626	.935571	.004320	.931251
y 1.193539	.021798	1.17182	.006661	1.165158
z 1.190448	.133309	1.057138	.025810	1.031328
p		1.257465	.148520	1.108944
q		1.280255	.187285	1.09297
r				1.04234
				1.324768

With only two electrons only one difference frequency is possible. With three electrons there are three possible differences, and with four electrons there are six possible differences between pairs of electrons. It is well known that the first Lyman line may appear alone, with excitation at the first resonance potential. If the second Lyman line is excited, requiring the second resonance potential or higher, it invariably is accompanied by the first Lyman line and the first Balmer line; while if the third Lyman line is excited, the first and second Lyman lines also appear, with two Balmer lines and one Paschen line — six lines in all. We may surmise that these lines may be emitted by the two-atom, the three-atom, and the four-atom molecules. With the Rydberg frequency taken as the unit, their respective frequencies would be

Atoms

Differences between Electrons

	<i>a-b</i>	<i>a-e</i>	<i>a-g</i>	<i>b-e</i>	<i>b-g</i>	<i>e-g</i>
2	.75					
3	.75	.8889		.1389		
4	.75	.8889	.9375	.1389	.1875	.0486

We now ask what would be required of the three line molecules if the three-atom molecule actually emitted frequencies of the two Lyman lines and one Balmer line, and if the four-atom molecule actually could emit any or all the frequencies assigned by the differences set forth in the above schedule.

For the three-atom line molecule the equations for frequencies of each of the three electrons reduce to:

$$\begin{aligned}\nu_a^2 &= \nu_0^2 \times \left\{ 1.79224304 + \left[.1806258 \left(1 - \frac{dz}{dx} \right) + .02008632 \left(1 - \frac{dq}{dx} \right) \right] \right\} \\ \nu_b^2 &= \nu_0^2 \times \left\{ 1.4205724 + \left[.1906258 \left(1 - \frac{dx}{dz} \right) - .14360136 \left(1 - \frac{dq}{dz} \right) \right] \right\} \\ \nu_e^2 &= \nu_0^2 \times \left\{ .12907865 + \left[.02008632 \left(1 - \frac{dx}{dq} \right) + .14360136 \left(1 - \frac{dz}{dq} \right) \right] \right\}\end{aligned}$$

For the four-atom molecule they reduce to:

$$\begin{aligned}\nu_a^2 &= \nu_0^2 \times \left\{ 1.836827 - \left[.188731 \frac{dz - dx}{dx} + .023504 \frac{dq - dx}{dx} + .006284 \frac{ds - dx}{dx} \right] \right\} \\ \nu_b^2 &= \nu_0^2 \times \left\{ 1.341619 + \left[.188731 \frac{dz - dx}{dz} - .187523 \frac{dq - dy}{dz} - .020148 \frac{ds - dz}{dz} \right] \right\} \\ \nu_e^2 &= \nu_0^2 \times \left\{ 1.062083 + \left[.023504 \frac{dq - dx}{dq} + .187523 \frac{dq - dz}{dq} - .139555 \frac{ds - dq}{dq} \right] \right\} \\ \nu_g^2 &= \nu_0^2 \times \left\{ .078868 + \left[.006284 \frac{ds - dx}{ds} + .020148 \frac{ds - dz}{ds} + .139555 \frac{ds - dq}{ds} \right] \right\}\end{aligned}$$

The ratios

$$\frac{dz}{dx}, \frac{dq}{dx}, \frac{ds}{dx}, \frac{dq}{dz}, \frac{ds}{dz}, \frac{ds}{dq}$$

are interdependent and unknown, but from the argument in Chapter 5 it appears probable that the effects of the electrons upon one another are not large in comparison with the effects of the ions, so far as frequency is concerned. We may find the general nature of the corrections required to the numbers 1.792243, etc., before extracting the square roots to obtain frequencies, the differences between which would give the hydrogen primary lines. This is done in the schedule on the next page.

This schedule is suggestive only, as I have as yet no direct evidence that any two or more lines emanate from a single origin. If all the electrons in a single line molecule combine to give rise to a single dominating frequency, the minor difference frequencies being inconsiderable, all the observed lines of the primary spectrum of hydrogen could be accounted for mathematically, as differences between molecular frequencies, compounded.

But if, as the schedule suggests, there are several possible molecular origins for frequencies corresponding to the various primary lines, the contributions from diverse origins differing very slightly in frequency — though they may differ greatly in intensity — fine structure in the lines that are

observed should be expected. The extent to which such fine structure could be detected by means at our disposal would depend not only upon our observing instruments but also upon the relative abundance of the several sources as well as the differences in stabilized frequencies, and this suggests that more or different fine structure might be detected in hydrogen lines from those stellar spectra in which the third and fourth Balmer lines are more intense than the first and the second, than under laboratory conditions, where the first and the second Balmer lines always are the most intense observable.

Atoms		Frequencies							
		Electron <i>a</i>	Diff.	Electron <i>b</i>	Diff.	Electron <i>e</i>	Diff.	Electron <i>g</i>	
1	$\nu^2 = R^2x$	1							
	Correction	0							
	Sum	1							
	Sq. root	1							
2	$\nu^2 = R^2x$	1.675476		.278521					
	Correction	-.013149		+.011068					
	Sum	1.662328		.289589					
	Sq. root	1.2893	.7512	.5381					
3	$\nu^2 = R^2x$	1.792743		1.142057		.129078			
	Correction	-.134915		+.181363		+.031241			
	Sum	1.662328		1.323420		.160320			
	Sq. root	1.2893	.1389	1.1504	.75	.4004			
4	$\nu^2 = R^2x$	1.836827		1.341691		1.062083		.078868	
	Correction	-.174499		+.197645		+.151874		+.044895	
	Sum	1.662328		1.530336		1.213967		.123763	
	Sq. root	1.2893	.0486	1.2407	.1389	1.1018	.75	.3518	

However, if the dominating frequency emitted by the three-atom molecule is the second Lyman line, and that emitted by the four-atom molecule is the third Lyman line, and if the Balmer and Paschen frequencies attributable to these frequencies in the schedule are of negligible intensity, Balmer and Paschen frequencies could still occur as difference frequencies of Lyman lines, although the original sources were in molecules of different configurations. That such is the case is suggested by the analysis of the secondary spectrum in Chapter 2 and its discussion in Chapter 13, in which it seems possible to account for thousands of the classified lines without ascribing to any line molecule more than one stabilized frequency limit.

Discussion of the sources of spectral lines cannot profitably be carried much farther on the basis of the atomic model that limits the number of lines to be accounted for to those of the primary spectrum. It is necessary to modify the model so as to be able to account for the many lined spectrum and for the irregularities in the primary system itself, for it is a well known

fact that if any primary line is measured as carefully as possible and its frequency used to calculate the Rydberg frequency for hydrogen, assuming the applicability of the simple Rydberg formula, the Rydberg frequency so calculated will not be exactly the same as if a different line had been selected as a basis for the calculation.

Before taking up the discussion of the modification in our model necessary to take account of the facts that thus far have been left out of consideration, let us inquire what effects should be expected to result from wide differences in pressure and temperature and intensity of excitation.

In laboratory experiments, where the volume of the gas is small, unless the pressure is exceedingly low, the collisions of molecules, whatever their character, must be frequent, and we would not expect very long molecules to have a chance to form. Therefore only a few of the Balmer lines could be expected. As a matter of fact, under the conditions of excitation which produce the many lined spectrum abundantly, the number of Balmer lines that are readily observable or recorded photographically does not exceed six or seven; but when the pressure is so low and the excitation so long continued that only the primary lines are observable, eighteen or twenty of them may be measured, the first and second being the most intense.

In the case of some stellar spectra, however, as many as thirty lines have been observed, and it is found that in some cases the third and fourth lines are more intense than the first. Does not this indicate that in such hydrogen stars the atmosphere where these lines are emitted must be very rare, there being plenty of time between collisions for the long molecules not only to form but also to acquire comparative internal quiescence?

When the pressure of the gas is high, the lines broaden. They may broaden so much as to merge. The effect is to increase the intensity of the continuous spectrum in the vicinity of the lines. The number of lines other than primary likewise increases with the gas pressure until all the lines become indistinguishable. It seems obvious that when the pressure is high, the lines, which are only approximately monochromatic, may be regarded as the tail ends of continuous but irregular spectra due to violent agitation in which molecular collisions play an important part; but that longer stabilized trains may be produced when the pressure is low and collisions are less frequent, especially if the excitation under the latter conditions is chiefly derived from absorption of radiation from without rather than from direct electron impact. This, however, is a subject that will be discussed in Chapter 14.

Chapter 12

An Improved Model of the Hydrogen Atom

The model atom which we have hitherto considered is capable of uniting with other similar atoms to produce line molecules which approximate an explanation of the primary spectrum of hydrogen; but it cannot account for the many lined spectrum or for the limit of the continuous spectrum in the neighborhood of wave number 117754. The first step in explaining the rest of the hydrogen spectrum must be to account for the upper limit of the characteristic continuous spectrum. We must modify the model to permit two configurations of the atom, one to account for the limit 109678 and one for the limit 117754.43, only one of which can occur at one time in a single atom. The atom is no longer supposed to be spherically symmetrical. This involves the supposition that the nucleus does not consist of a single particle but of a combination of particles.

For this immediate purpose it is adequate to regard the nucleus as composed of three particles, each the center of an electric charge. The central particle will be assumed to possess most of the mass and to have a distributed negative charge $-e\left(1 + \frac{r_0}{r}\right)$, and the other two particles will be assumed to be positive electrons each of charge $+e$. The net charge will be $+e\left(1 - \frac{r_0}{r}\right)$ to objects at appreciable distances under conditions to be defined, as in our preliminary model.

The arrangement of the nuclear particles with respect to a poised "external" electron is indicated diagrammatically in Figure 11a and 11b. That indicated in Figure 11a I shall call the *a* configuration and that indi-

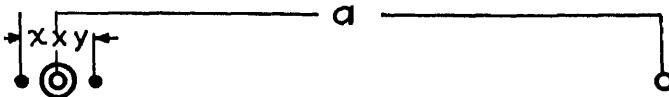


FIGURE 11a

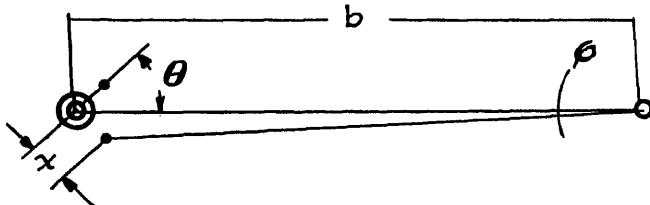


FIGURE 11b

cated by Figure 11b I shall call the *b* configuration. In the *a* configuration all three nuclear particles and the external electron are in the same straight line, but in the *b* configuration the nuclear particles are displaced by the attraction or repulsion of the external electron in such a manner as to bring both the nuclear electrons closer to the poised electron than to the negatively charged particle. It is obvious that if the nuclear particles also are poised (according to some law we are not now discussing), they will be displaced somewhat, differently in the two cases of alignment, and that the displacement will most likely be greater in the *b* configuration than in the *a*, assuming without proof on *a priori* grounds that both configurations are physically possible.

In Figure 11b let r_x represent the distance between the center of a positive electron and the center of the negative nuclear particle, and θ the angle between a line drawn through the center of the positive electron and the negative nuclear particle and a line through the center of the nuclear particle and the poised external electron. The distance between the negative nuclear particle and the poised external electron is indicated by r_b , which is very much greater than r_x , and the angle ϕ is so small that for our present purpose, which is an approximation, we shall neglect it. Then $r_b - r_x \cos \theta$ is very nearly the distance between the poised electron and the positive particles within the nucleus. If neither the positive electrons nor the poised electron act otherwise than as if their entire charges were concentrated at their centers, the force of attraction between the positive nuclear electrons and the poised electron would be

$$F_1 = \frac{2e^2}{(r_b - r_x \cos \theta)^2}$$

and this must be counterbalanced by the repulsion between the negatively charged nuclear particle and the poised electron. If r_0 has substantially the same significance as in our former model, this repulsion must be

$$F_2 = \frac{e^2}{r_b^2} - \frac{e^2 r_0}{r_b^3}$$

Therefore the condition necessary for poise is approximately

$$\frac{2e^2}{(r_b - r_x \cos \theta)^2} = \frac{e^2}{r_b^2} - \frac{e^2 r_0}{r_b^3} \quad \text{or} \quad \frac{2}{(b - x \cos \theta)^2} = \frac{1}{b^2} - \frac{1}{b^3}$$

from which we could find $x \cos \theta$ if we knew b .

For trial purposes we will take for b the quantum number of the limit 117754, which is .9651 (see Chapter 2), which gives us $x \cos \theta = .0089$. Since $\cos \theta$ cannot be greater than 1, x cannot be less than .0089, if there is to be stability, under the conditions specified for the purposes of exploration. Thus far we have considered only a solitary atom. However, it is obvious that if several atoms are in line, the nuclear configurations will be modified, although not to the same extent for all line molecules.

In the case of the *a* configuration, not knowing the law by which the nuclear particles are poised with respect to one another, we will assume

that it permits only small displacement of the positive nuclear electrons from the negative center, and that the radial displacement may be ignored for preliminary purposes. In Figure 11a, let $x = y = .01$ — a little greater than the minimum .0089 found for the other case. The force exerted upon the external negative electron would then be

$$F = \frac{e^2}{r_0^2} \left[\frac{1}{(1+x)^2} + \frac{1}{(1-y)^2} - \frac{1}{a^2} \right]$$

which must be zero when the electron is poised. Solving for a , we find $a = .999$, which differs so little from 1 that the discrepancy between the assumption made with our former model, that all the nuclear charges are concentric, and the implications of this model is very small, and may even eventually serve to assist us in determining the actual configurations or to correct this model if it still is defective as well as incomplete.

Chapter 13

The Origins of the Many Lined Spectrum

The improved atomic model described in Chapter 12 enables us to account schematically for the numerous lines hitherto called "secondary" and ascribed by quantum theory to "the molecule." If it be assumed that hydrogen molecules of the two common forms known to occur in the gas at ordinary temperatures and pressures are broken up by electrical excitation into atoms of both *a* and *b* configurations, if the pressure within the containing chamber is low enough to insure that collisions are not too frequent, the formation of line molecules containing atoms of both configurations is to be expected. These molecules may be designated by various combinations of the letters *a* and *b*, such as *ba*, *bb*, *aa*, *bba*, *bbb*, *aba*, *abb*, etc., according to the schedule used in Chapter 2 to designate the various "levels" evaluated by mathematical analysis.

But the investigations in Chapter 10 and 11 indicate that such molecular combinations of atoms in the *a* configuration must give rise to at least partially stabilized frequencies corresponding to the Lyman lines, and not to the levels used in classification. Thus the wave number of the Balmer level is given by the "combination" (*a* = 109678) - (*aa* = 82158.50) = 27419.50, instead of the line 82158.50 by the combination 109678 - 27419.50, as demanded by Bohr's theory. By analogy the molecule *bb* should be expected to produce a stabilized or partially stabilized frequency corresponding to wave number 117754.43 - 29326.52 = 88427.91; and the "level" 29326.52, however useful it may be in classification by means of series formulas, does not represent an actual physical state of any one body, be it atom or molecule.

Therefore, in Table 73 I have arranged a part of Table 1 in a manner which indicates also the true wave number limits of the various molecular configurations, instead of the classification levels only. In this rearranged table the designation of the molecule is the same as the designation of the level in Chapter 2. It is given in the middle column. In the next column to the right is the level, in wave numbers, as in Chapter 2, and in the column to the left is the molecular limit, in wave numbers. These numbers for a single atom are the same as the levels in the two atomic configurations *a* and *b*; but in all other cases they may be obtained by subtraction from the wave numbers of *a* or *b* the wave numbers of the classification level. For instance, the molecular limit assigned to the molecular *ba* is 82379.15 = 117754.43 - 35375.27. I have not calculated any of these molecular limits

by the method used in Chapters 10 and 11, for the reason that the molecular dimensions are not yet sufficiently well known to make such calculations possible, if accurate results are demanded.

The differences given in the left-hand side of this table could arise by the cooperation of pairs of molecules, without the assistance of solitary atoms. They include the 0-0 nulls of the most intense band systems which develop at comparatively low pressure and the most important differences from null to null in the various band systems. All the most regular band systems are among these. The differences in the right-hand side of the table can all be accounted for as differences between molecular limits plus the difference $b-a = 8076.43$, or as differences between the classification levels, which apparently are conveniences merely.

By way of example certain nulls which in classification are regarded as differences between levels now are regarded as equally simple differences between molecular limits, thus:

<i>Level differences</i>	<i>Wave no.</i>	<i>Molecular differences</i>
$ba-bbaa$	21621.84	$bbaa-ba$
$bb-abb$	16619.01	$abb-bb$

But other differences, classifiable as simple differences between levels, must be assigned to compounding of differences from several sources, thus:

<i>Level differences</i>	<i>Wave no.</i>	<i>Molecular differences</i>
$b-aa$	90334.93	$aa + 8076.43$
$ba-aaa$	27188.83	$aaa-ba + 8076.43$
$bb-aaa$	16891.42	$aaa-bb + 8076.43$

In Table 73 the number 8076.43 is ascribed to the difference $b-a$, a difference between atomic rather than molecular limits.

These molecular limits all are in the Schumann region, although the possibility that one molecule possessed of more than two poised electrons, as discussed in Chapter 11, may be responsible for more than one stabilized frequency has not been eliminated, though seemingly not necessary. The smallest wave number assigned to any single molecule is the first Lyman line, 82258.50, assigned to aa . Next comes the wave number 82739.06, assigned to ba , and next 88427.91 assigned to bb . The only lines that are observed as possibilities for a single molecule are those of the Lyman series. All the other lines require the cooperation of two or more bodies to produce sufficient stabilization to give rise to a spectral line. However, from this fact derived from mathematical classification only, we are not justified in assuming without further proof that completely stabilized frequency may be attained within a single molecule without the cooperation of others. I do not myself believe that any completely stabilized frequency can be produced by a single source, or that if such complete stabilization in one source could be attained, the radiation therefrom could have intensity sufficient to record itself on a photographic plate.

In the infrared region our information does not extend to lines having wave numbers less than 11230 or thereabouts, that being the smallest wave number recorded in Gale's tables. The simplest "combination" of two sources that could be expected is $b-a = 8076.43$.

In the band systems in the visible region, with which we are most familiar, and for which the classification of band lines is most complete and accurate, the number of subordinate nulls indicates that in most cases a line requires many combinations before comparative monochromatism is attained in long enough trains to be recordable photographically as spectral lines. It seems to me very probable that not only in the case of hydrogen but in all line spectra the sharp lines which apparently are produced by very long wave trains, because they are capable of producing interference with intervals of thousands of waves between the interfering impulses, require the cooperation of many sources. According to Michelson, interference can be observable in some cases between impulses that are separated as much as five hundred thousand waves in the train. It must require a great many molecular or atomic sources, cooperating by mutual absorption and reemission, to produce such trains, of sufficient intensity to have appreciable physical effects at great distances, when gathered together by optical instruments. If the molecules are not all exactly alike, there are to be expected multiplications of differences of precisely the same kind as that called the Raman effect, when light from one source is passed through material different from its source. This is the physical cause of "band" structure, resulting in great multiplicity of lines. In the special case of the primary spectrum the number of varieties of molecules is limited, and in consequence the number of possible lines limited; but as the wave numbers of the lines do not follow strictly the simple Rydberg formula, there are several physical combinations which can give rise to lines of almost the same wave length, but not exactly the same. The result to be expected is fine structure.

If reference is made to Table 1, it will be observed that certain "levels" play a much more important part in the classification of the various band systems than others. From this it is to be expected that those molecules which are responsible for these particular levels are especially plentiful under the conditions which develop the band systems which reveal these levels by analysis. How, then, are the molecules responsible for these levels formed, and why are some more plentiful than others?

In the normal unexcited state, hydrogen gas is known to contain molecules composed of two atoms each; but there are at least two configurations, which occur mixed together, the proportions depending upon the temperature, pressure, and previous condition of the gas. The increase of temperature causes the increase of number of molecules of one form at the expense of the other, while lowering the temperature causes a relative increase of the other. If hydrogen that has been evaporated from activated carbon in which it has been absorbed at liquid air temperature is excited electrically, those band lines which, according to our analysis, require the molecules

bb, *bbb*, and *bbbb* for their development are more intense than lines which do not require these molecules or the "levels" associated with them in our analysis. It would seem, therefore, that one of the molecular configurations of normal hydrogen gas is more readily converted into the form *bb* or broken up in such a manner as to give rise to atoms in the *b* configuration than the other.

We also notice in Table 1 that no level is found that may be assigned to the molecule *ab*, but that levels are assigned to the molecules *ba*, *bb*, and *aa*. From this it seems probable that, in the process of excitation, not all molecules are dissociated into atoms of the two configurations, but many are merely opened up from the closed molecular forms into the line forms, the forms *ba*, *bb*, and *aa* resulting, though not the form *ab*. The immediate result of electrical excitation would then be the formation of three varieties of line molecules of two atoms each, and this would be followed or accompanied by the formation of separate atoms of both configurations. Thereafter, single atoms could combine with the two-atom line molecules, producing all the eight forms found in our schedule; these in turn could acquire additional atoms at either end, producing all the forms of four-atom line molecules provided for in the schedule. But the two-atom molecules also could unite with one another, producing four-atom molecules. The number of possible configurations that could be formed in this way would not include any terminating with the combination *ab* or beginning therewith. Thus there would be nine forms that could occur in this manner instead of sixteen that could occur by the accretion of single atoms one at a time. These preferred forms are:



It is of special interest to note that these levels play a most important part in the development of the more regular band systems. In the case of hydrogen, whether or not in other cases, the characteristic spectral lines do not appear until there have been changes in the normal forms of the molecules; but these changes once instituted, excitation of characteristic spectra can occur by electron impact or by absorption of radiant energy of suitable character from without.

Normal hydrogen gas at ordinary temperatures has a critical potential that is not associated with any series limit or any special spectral line. This potential is in the neighborhood of 16 volts but is not sharply defined, and its interpretation was subject to much controversy some twenty or more years ago, the prevailing opinion then being that this potential represents dissociation plus ionization. The estimates of voltage assigned to this compound reaction varied from 15.8 to 16.4; and as the ionization voltage associated with the primary spectrum was known to be very nearly 13.54, this left between 2.26 and 2.86 volts to account for dissociation. At that time it was not known that there are two forms of hydrogen molecules in the normal gas, which would require two critical potentials for the change, whatever

it may be. If there are, however, also two configurations of the atom, which I have designated *a* and *b*, the latter requiring a higher potential to ionize directly, if the usual explanation is correct, the critical potential observable depends very largely upon the condition of the gas before the observations are made. Another explanation, however, seems more probable — that this critical potential represents not ionization and dissociation combined, but the opening up of the normal molecules (two forms) into line molecules of different configurations, and that ionization, which requires less voltage when the atoms are separated, is a subsequent step.

Chapter 14

Excitation of Emission Spectra

Both continuous and line spectra may be excited by heating a body, by bombarding it with electrons from without, or by subjecting it to radiation such as light or x-rays.

If heat is the exciting influence, the shortest wave length or maximum frequency attainable is fixed by the temperature; and since in the laboratory it is impossible to attain temperatures of more than a few thousand degrees, the shortest wave lengths and highest frequencies attainable by heating do not exceed those given by electron bombardment of two or three volts potential.

If excitation is accomplished by electron streams, it is possible to use potentials as great as several hundred thousand volts, which makes it possible to produce radiation in the x-ray regions. The radiation obtained by electron bombardment at high voltages may in turn be used to excite "secondary" targets, without electron bombardment from outside sources. Radiation resulting from the impact of x-rays is due in part to the behavior of electrons already in the target, set in motion by the incident radiation, and in part to reflection of incident radiation with or without change in the character of the pulses of which it is composed.

This is true also of the radiation produced in a target subjected to electron bombardment from without. In that case there are two sets of pulses to be considered; first those pulses resulting from the behavior of the invading electrons, and second those pulses resulting from the behavior of the electrons within the target.

The number of electrons associated with the atoms of a target of appreciable size must be very great in comparison with the number of invaders in the target at a given instant. Consequently, it is reasonable to suppose that even when excitation is occasioned only by streams of electrons accelerated by high voltages impinging upon the target, most of the pulses are due to the behavior of the electrons normally in the target and not to the invaders, which initiate the disturbances.

Before discussing the pulses of radiation which electromagnetic theory insists would accompany otherwise elastic collision of electrons with ions, let us consider the mechanical results to be expected from elastic collisions, if there were no radiation. The target against which electrons impinge contains two kinds of particles — ions and electrons. Some of the ions are much more massive than others, but the least massive of all, the hydrogen atomic

ion, is more than 1800 times as massive as the electron. According to the laws of impact, an electron making direct collision with another electron at rest could impart to it all of its own kinetic energy and come to rest, assuming that the collision were perfectly elastic. But if it collided directly with an ion 1800 times as massive as itself it would rebound, the relative velocities of electron and ion being inversely proportional to their masses. If the ion were at rest prior to the collision it would have imparted to it about 1/1800 of the kinetic energy of the electron after collision. It is obvious that since a target bombarded by electrons contains both electrons and ions, the kinetic energy imparted to the target electrons by bombardment of electrons from without will be many times as great as that imparted to the ions, and that if the target is a solid, the energy imparted to the surface electrons will be much greater than that imparted to electrons deeper within the target.

If the source of excitation is pulses of radiation the electrons within the target will be much more affected than the ions; but in comparison with the energy of a moving electron, the energy of a single pulse of the nature of light is very minute. Consequently, to produce comparable effects ordinary light pulses must be vastly more numerous than bombarding electrons. In most cases the energy imparted to an electron by a single pulse of the nature of ordinary light must be so small that a vast number of such pulses must act cumulatively to produce an observable effect; for an effect, to be observable, must be stable, not merely a minute disturbance, resulting in radiation immediately following without any time interval between.

It is generally known that the "frequency" of radiation, judged by spectroscopic standards, is limited by the excitation voltage imparted to the exciting electrons. Frequency is calculated from wave length, which is determined from the position of spectral lines of limits, usually on a photographic plate, where they may be measured and compared. Use of this terminology does not imply that in a continuous spectrum there is any actual monochromatic wave train of the calculated frequency, but only that the point on the spectrum so designated is the same as if a line, the frequency of which could be calculated from the wave length, were observed there. Bearing this in mind, the relationship of the limiting frequency to voltage of electron bombardment may be expressed by a formula derived directly from observation. If V is the potential in volts and ν the frequency in wave numbers

$$\nu \div V = 8100 \text{ (approx.)}$$

However, if ν is oscillations per second and V is expressed in cgs units, this formula may be written

$$\nu \div V = e \div h$$

in which e is the charge of the electron at rest and h is Planck's constant. There is no dispute about the fact that this formula is substantially correct.

Quantum theory writes this equation in another form, introduces another

term and interprets it as representing transformations of energy from a potential form to a kinetic form, and from that to radiation. The equation is

$$eV = \frac{mv^2}{2} = h\nu$$

in which m is the mass of the electron moving with the velocity v ; v its velocity after acceleration by the potential V ; and $h\nu$ is a quantum or photon of radiant energy which moves with the velocity of light and is unaffected by electric and magnetic fields.

I do not entertain this assumption, or consider that a moving electron can part with its kinetic energy except mechanically, or as radiation in pulses in conformity with electromagnetic principles. According to my views, an electron encountering a target must either rebound elastically or penetrate the target, in which case it will make innumerable collisions, or close approaches to ions and other electrons, and thus eventually reduce its average kinetic energy to that of the other electrons of the body.

In Chapter 8 is a discussion of the nature of pulses to be expected to occur in sequence in wave trains emitted by oscillations of an electron about a poised position in our simplified ideal hydrogen atomic model. The formula for force exerted between the ion and the electron there considered is:

$$F = \frac{e^2}{r^2} - \frac{e^2 r_0}{r^3}$$

If an external electron invaded this structure it would be opposed by the resident electron, and also by the ion itself if it succeeded in penetrating closer to the ionic center than the distance r_0 ; but in that ideal atom, the resident electron is movable.

In neutral atoms of large atomic number doubtless there are many electrons within the structure, much closer to the center than the distance r_0 . The force resisting invasion by another electron would therefore approximate more closely the formula

$$F = \frac{e^2 r_0}{r^3}$$

as the atomic number and the penetration were increased. We will assume this formula as an approximation for atoms of high atomic number where the large voltages are used to accelerate the invader. Then, since

$$F = \frac{e^2 r_0}{r^3}, \alpha = \frac{e^2 r_0}{r^3 m} \quad \text{and} \quad W = \int_r^\infty F dv = \frac{e^2 r_0}{2r^2}$$

is the work that must be done on an electron to cause it to penetrate the ideal atom of larger atomic number to the distance r from its center. This must be the kinetic energy of the invader, before its approach, from which $r^2 = \frac{e^2 r_0}{2W}$ gives the maximum penetration possible by an electron moving

with kinetic energy W . Designate radiation intensity by I . Then by ordinary electromagnetic theory

$$\frac{dI}{dt} = \frac{2}{3} \frac{e^4 \alpha^2}{c^3} = \frac{2e^4 r_0^4}{3c^3 m^2 r^3} = \frac{16W^3}{3c^2 m^2 r_0}$$

is the rate of energy loss by radiation at the instant the electron attains its maximum penetration. The maximum possible rate of radiation in a pulse produced by electron bombardment therefore is proportional to the third power of the kinetic energy of the invader before impact.

It will be noticed that this treatment does not require discussion of relativity theory because the mass m in the foregoing equation is the mass of the electron at the instant of rest. How the kinetic energy, W , is imparted to the electron also does not enter the problem; nor does the velocity of the electron before impact need consideration.

Only the maximum rate of radiation of a pulse produced by most favorable impact is given in the last equation. If, however, both charge and mass of the electron are considered constant, the distribution of energy in the pulse may be calculated by methods similar to those used in Chapter 8, provided the energy of the pulse is not too large a part of the total energy of impact. In form a graph of the pulse would resemble Figure 3 (p. 84), but with the entire curve above the base line.

The target consists not of a single atom, but of a very great number of atoms, in the form of a solid, a liquid or a gas. The invading electron would rebound in the opposite direction from which it came only if the first impact were radial to an individual atom. If that impact were oblique, a pulse of less intensity would be produced, but the electron would penetrate the target and undergo numerous other collisions, radiating some energy at each collision.

In the foregoing, only pulses of the radiation produced by the invader have been considered, ignoring the effects upon electrons in the target, which especially in the case of a solid target must be many times as numerous as the invaders. These resident electrons would have motion imparted to them both by direct approach of the invader and by absorption of some of the energy of the pulses produced by the invader. Therefore, electrical excitation of atoms and molecules must be attributed both to direct electron impact and to absorption of pulses produced by retardation and reaccelerations of the invading electrons. There should be a great similarity between spectra produced by electron impact at given potentials and spectra resulting by the absorption of light or x-rays of wave numbers corresponding to those potentials.

The continuous spectrum produced by heat — that due to temperature alone — should be expected to differ in its energy distribution from that produced by electron bombardment, for two reasons. The first reason is that the pulses are produced by accelerations and retardations of all the electrons within the heated body, because both electrons and ions are in a

state of agitation due to the temperature, and there must be all degrees of kinetic energy which the temperature is able to produce, all conditions being taken into account. What we call "sensible" heat is due to motions of bodies relatively to one another and capable of communicating motion to one another by elastic impact, which on last analysis doubtless is electrical in nature.

As a mathematical proposition, if all the particles in a gas were perfectly elastic, their number infinite, and simple probability laws applied, as in a perfect ideal gas, and there was no radiation, some of the particles could attain infinite velocities, though the number would be vanishingly small. However, if the particles are electrons and ions, or similar bodies, this cannot be true; for each collision results in radiation, and the greater the kinetic energy of the colliding particles, the larger the portion of energy that is converted into radiation. The maximum possibility is proportional, as we have seen, to the cube of the kinetic energy of the electron with respect to an atom with which it collides.

Thus the electrons themselves cannot possibly attain those velocities which the simple theory of an ideal gas would allow them. A maximum velocity which electrons may attain is thus fixed by the temperature. The energy of the pulses, however, need not escape if boundary temperatures are maintained, for it is re-absorbed by neighboring electrons. Consequently, as is well known, there is a temperature which corresponds to voltage of impact of an electron stream in its ability to excite a spectrum of given maximum frequency. This is about 2336°C on the absolute scale per volt. Planck has given us the laws of distribution in the continuous spectrum resulting from temperature alone. There is nothing in his mathematical treatment of this matter which is in the least contradictory to electromagnetic theory. Planck, however, did not approach the problem by considering the nature of pulses, but, for the sake of mathematical convenience alone — since mathematically (though not necessarily physically) individual pulses may be regarded as resolvable into series of vanishingly small monochromatic wave chains — he preferred to follow the unsuccessful treatments of Wean and Rayleigh, and to correct their formulas by a modification introducing his constant, h , which he was able to evaluate from empirical data.

It is now necessary to show the fallacy in the assertion of advocates of quantum theory that a continuous spectrum produced by heterogeneous pulses could not have a sharp upper limit, and that the fact that observed continuous spectra do have sharp high-frequency limits proves they could not be due to pulses. The argument in favor of this opinion is somewhat as follows:

"Any pulse, no matter how complicated, may be regarded mathematically as composed of a number of individual pulses of uniform character superimposed upon one another. By Fourier series, every uniform pulse is mathematically equivalent to an infinite number of wave trains, each of

constant frequency, but individually differing in frequency from zero to infinity. Consequently, the spectrum of any number of superimposed pulses, whatever their individual character, must extend from zero to infinite frequency. All observed continuous spectra have definite high-frequency limits. Consequently, continuous spectra cannot be due to pulses."

This argument completely overlooks the fact that the amount of energy contained in an individual pulse such as we are considering is ordinarily such a minute portion of the total kinetic energy of any electron producing it that at best it could displace an electron in a neighboring atom only an exceedingly slight amount. In order that the displacement may produce an observable effect, it must be of sufficient magnitude to result in at least temporary stability, in a new configuration. For example, if the effect is in a photographic film, it must be of such stability as will enable a developing process to amplify it so that it may be seen. Very many minute pulses, cumulatively, would be necessary to produce such an effect. The matter of mathematical equivalence of pulses resolved into infinitely more minute trains of pulses, each of vanishingly small magnitude, has no bearing whatever upon the problem, for such minute, vanishingly small trains have individually negligible energies.

According to electromagnetic theory, the energy per unit area of wave front of a pulse from a distant source diminishes according to the inverse square of the distance from the source. Let us consider for a moment how very minute must be the energy reaching the small area of a photographic lens and focused upon a sensitive plate, the origin of which is an atom of hydrogen in the atmosphere of the sun! The energy which affects the plate must have been derived from vast multitudes of pulses or of wave trains, acting cumulatively by a mechanism to be discovered.

If light and x-ray pulses are of the general character of those attributed to the electron oscillating in the hydrogen atom, as discussed in Chapter 9, each such pulse would communicate to an electron which it encounters a push in a certain direction only. A sequence of like pulses coming from the same direction would produce a sequence of similar pulses in the same direction. If the electron were perfectly free it would be accelerated by each pulse and would acquire velocity. This would occur whether the pulses arrived in regular, equally spaced sequence or entirely independently of one another in time. Pulses of the same character from any number of different sources in the same general direction from the electron accelerated would have similar effects. How great a velocity could such pulses impart to the electron if it were entirely unrestrained by neighboring atoms or ions?

This is a crucial question, but I think that it can be answered without violence to electromagnetic theory. Although each pulse is propagated from its source with the velocity of light, and arrives at the electron from a certain direction, it does not impart to the electron any push in its own direction, nor is its velocity affected. The push which it gives is at right

angles to its own travel, and does not affect its own velocity. The pulse suffers a loss in giving the push, but the loss is not merely one of energy, but also one of sharpness or shape.

It is necessary to recognize that each pulse, no matter how feeble it may be if measured over a given area owing to the distance from its source, has a character of its own, which is not modified in the process of transmission. This character may be called shape, or sharpness. The sharpness is not the same throughout the entire pulse, but there is a maximum sharpness which is a property of each pulse, and which limits its ability to impart a push to a moving electron. If the electron is already moving in the direction in which the pulse would push it if it were at rest, the "sharpness" of the pulse must be such as to catch up with the electron, as it were, and give it a shove. It is not mere intensity, but sharpness which is required to increase the velocity of an electron in the direction in which it already is moving.

Therefore, the maximum velocity that can be imparted to an electron by innumerable pulses of like kind in like direction is limited by the character of the sharpest pulses which the radiation contains, whether the pulses are arranged in regular or random sequences.

If the electron is not free, but is poised in an atom or molecule in such a way that forces tending to restore it to normal position arise if it is deflected therefrom, while any pulse may give it a push, a succession of pushes may not be able to overcome the forces of restitution. If, however, the electron is poised in such a manner that with very small amplitude it may oscillate about the position of equilibrium at approximately constant frequency, a succession of pulses in regular sequence may, by resonance, increase the amplitude of oscillation. The pulses, however, must not only be properly spaced in time, but also must be of both adequate sharpness and sufficient intensity to be effective. This is resonance.

Although pulses arriving in irregular sequence and in different phase relationships to any oscillating electron would not all produce cumulative effects upon the amplitude of oscillation of that particular electron, pulses having broad fronts affect many electrons in the same target, and each pulse arriving at the target increases the agitation of the electrons therein, on the whole, as a result, the distribution of kinetic energy among the target electrons must follow some law of probability; if the total energy arriving is sufficient, and the character of pulses is also sufficient, the only limit to the velocity which some electrons may acquire is fixed by the sharpness of the pulses. When all the impacting electrons have been accelerated by the same voltage, that voltage, plus threshold intensity, must fix the limit of the continuous spectrum to be expected.

If the bombardment by electrons is sufficient, directly or indirectly, to disintegrate some of the atoms in the target into some of their sub-atoms, there result not only continuous spectra but also characteristic spectra. In addition to the continuous spectrum with a limit determined by the

excitation voltage, if the target contains atoms of sufficiently large atomic number, there may be both spectral lines and continuous spectra the limits of which are determined by the sub-atoms and not by the excitation voltage. Such is the characteristic continuous spectrum of hydrogen discussed in other chapters of this book. Characteristic spectra are not due to heterogeneous pulses, but to pulses arranged in trains, which may be of varying frequency or approximately constant frequency because stabilized by some supply of energy to replace that lost by radiation.

It seems to me that the evidence indicates that spectral lines result only when their original sources are line molecules in which sub-atomic ions and electrons are arranged alternately in substantially straight lines, so that the radiation emitted when received at a distance resembles that which would be expected if a single charge were oscillating at constant frequency, rectilinearly. Very many such original sources, not necessarily in parallel lines, contribute to the spectral lines actually observed. Of course these line molecules are not stationary, but move in various directions, and may be differently oriented, the orientations and motions being affected by electric and magnetic fields; for in most cases these molecules are not neutral, but are ions of various positive charges.

This hypothesis does not imply that only line molecules emit radiation, but merely that these are the bodies which are responsible for spectral lines. This is in keeping with the fact that solar radiation is heterogeneous in character, although a vast number of spectral lines are observed as absorption lines.

The atoms known to the chemist are combinations that normally are stable at ordinary temperatures under terrestrial conditions. If they contain such sub-atoms as I have suggested, there must be not only the sub-atomic ions but also many electrons within the atomic structure of a neutral atom of large atomic number. The number of electrons required is equal to the sum of the atomic numbers of the sub-atomic ions in the structure. Most of these must be required to hold the ions together, and are not near what may be called the surface. A few, however, are sufficiently far out to affect the chemical properties, and to be at least partially responsible for valence.

In the process of excitation that produces spectral lines, the sub-atoms of small atomic number are separated from the atom as a whole, probably with only a single electron accompanying each. The sub-atoms of higher atomic number remain together unless the excitation is sufficient to separate them also, but with fewer electrons binding them together. Not merely single electrons are released one at a time in the process of excitation, but as many as necessary to separate the sub-atoms from one another completely.

While I have described this scheme and treated it in some detail for hydrogen only in Chapters 8 to 13, to extend it to other sub-elements it will be necessary to show that sub-atomic ions of larger atomic number

follow the same general pattern as has been applied to hydrogen, and that the proposed combinations of such sub-atoms are possible without abrogating electromagnetic or electrostatic laws. I shall attempt this in Chapter 15, which deals with nuclear structure.

Let us simplify the problem of excitation by electron impact by considering the result of such impact upon a simplified hydrogen atom such as discussed in Chapter 8. The possible results are as follows:

- (1) The invader might be captured, producing a negatively charged atomic ion.
- (2) The invader might expel the resident and take its place.
- (3) The invader might expel the resident and itself pass out of the atom, leaving a positive ion.
- (4) The invader might rebound, or pass through the atom, leaving the resident either undisturbed or in a state of oscillation.

We shall consider these possibilities in the order stated above.

We know from Aston that negative atoms of mass number 1 are revealed by mass spectroscopy, but that they are not plentiful in comparison with positive ions of the same mass number. This would not be possible for an atom constructed after the original Bohr model or the preliminary model discussed in Chapter 8, because in order to be stable in either of those models the electrons would both have to be at an infinite distance from the ionic center. The case is different for the improved model discussed in Chapter 12, in which two electrons could be poised opposite each other on the *a* axis at equal distances from the center of the ion.

If the invader expelled the resident and took its place, without retaining any surplus kinetic energy, the resident would leave the system with the same velocity as that with which the invader entered it. On the other hand, the resident might be expelled and the invader retain some residual kinetic energy, which would cause it to oscillate about a position of poise. This is one form of excitation by direct impact.

If both electrons left the system, there could be no oscillation until another electron was captured by the ion.

The invader might pass through the atom so rapidly as to displace the resident, but not expel it. In such an event there are two possibilities. The displacement might be merely while the invader was passing, the resident returning to its normal position of poise without residual kinetic energy; or the invader might pass through the atom so rapidly that the resident was displaced somewhat, not expelled, but did not return to its poised position before the invader had passed. This would be another form of excitation by direct impact.

The tracks of negative electrons in Wilson cloud chambers seem to me to prove conclusively that very rapidly moving electrons do expel other electrons from their normal positions in the molecules of the gases in the cloud chambers. Ionization by direct impact must therefore be one of the results that cannot be questioned.

These various forms of excitation must be common to other atoms and molecules, but they are complicated by the complex structures, which are altered by the loss of electrons, whether by direct impact or indirectly by the absorption of radiation.

If the configurations within the target are suitable, in addition to the non-characteristic continuous spectrum the target will also emit characteristic spectra, which may be either continuous or monochromatic, depending upon the behavior of the matter in the target undergoing the process of readjustment. Thus, the continuous spectrum of hydrogen and that of helium, which provide radiation sources for observation of various absorption spectra, are for the most part *characteristic* spectra, though non-characteristic spectra accompany them.

The processes of excitation which produce characteristic line spectra involve much more than displacement of electrons. The complex molecule and atom in the target, whatever it may be, must be modified and the parts recombine partially in other configurations of such character that stabilized frequencies are possible. At the present time there is considerable knowledge regarding excitation of spectra after the bodies necessary for emission have been produced, but comparatively little regarding the preliminary steps by which the atom or molecule is separated into component parts and the parts recombined to produce the bodies responsible for characteristic emissions — those responsible for the spectra of different orders.

We must now account for the fact that x-ray lines may be altered by reflection. From the discussion of the continuous spectrum of hydrogen in Chapter 9 it is evident that it is possible for pulses to follow one another in regular sequence, but with their crests not spaced at equal intervals of time. It is obvious also that the shape of an individual pulse is not a portion of a sin curve, whether the pulses are equally spaced or not, and that all pulses are not alike, even if they are equally spaced in time. In the hydrogen atom, the greater the amplitude, the longer the interval between peaks, but also the sharper the individual pulses at the peaks. Only when the amplitude is vanishingly small does the oscillation approach simple harmonic motion.

From the considerations discussed in Chapter 9 it is clear that when two ions have an electron oscillating between them, a part of the energy of the system lost by radiation may be supplied to maintain approximately constant frequency by closer approach of the ions to each other. Though the pulses are not all alike under such circumstances they may be equally spaced in time, and such a wave train may produce observable interference. In the x-ray region the pulses are very much sharper than in the visible region, and the sharpness of individual pulses must be relatively more important in determining how they are deflected by various optical devices than in the visible region where the pulses are less sharp.

If a *K* line of the x-ray spectrum of an element of large atomic number consists of a series of equally spaced pulses of equal sharpness, or approxi-

mately so, each pulse would be deflected or dispersed in like manner by the same optical device. The degree of displacement would depend only upon the optical system, but the pulses would follow regularly spaced in time, and therefore could produce on a photographic plate a spectral line, the position of which can be measured. Let us now suppose that we have some means by which the character of each pulse may be changed, but not the sequence of the pulses, or true frequency of the wave train. Undoubtedly the crests of the pulses would be shifted differently, but there still would be the necessary interference to produce a spectral line, the position of which would not be the same as that of the line occasioned by the chain of unmodified pulses.

A pulse may be modified by imparting acceleration to an electron, and there are electrons in all forms of matter. It should not surprise us, therefore, if x-ray lines are shifted upon reflection. This shifting and duplication of x-ray lines upon reflection is known as the Compton effect. It has been the subject of a great deal of experimental investigation and theoretical interpretation. A very comprehensive account of it is given in Compton and Allison's book, "X-rays in Theory and Experiment," the last printing of which was in 1946. Compton attributes the shifted line to an actual change in frequency of a train of waves (a photon), while I attribute it to a loss of sharpness of individual pulses constituting a train. I agree entirely with Compton in ascribing the shift to absorption of energy of radiation by electrons in the secondary target.

Although in the laboratory the Compton effect has been observed only in x-ray spectral lines, in which the pulses must be very sharp, there is no reason for assuming that this effect is impossible in the region of visible light, although it has not been observed in optical spectra. A speculation about one of the phenomena that has puzzled astronomers may be permissible, because of its possible connection with the Compton effect. If there are free electrons or other charged bodies in the space traversed by light between us and distant stars or nebulas, they must have imparted to them pushes by any radiation pulses which pass them. These pushes, however small they may be, affect the sharpness of the passing pulse, whether it be a member of a train or unrelated to other pulses. If the charges are distributed with some statistical regularity in space, the damping would be proportional to the distance. If my suggestion about the Compton effect is correct, the shifting of spectral lines from very distant sources toward the red may be another manifestation of the Compton effect which we observe in the laboratory only in connection with pulses many times sharper than any of the pulses responsible for optical spectra. At the present time speculative theory ascribes this shift of lines from distant sources to an "expanding universe."

Chapter 15

Nuclear Structure

It is with some hesitation that I publish the thoughts about nuclear structure and other matters of a speculative nature which my studies of spectra have suggested, because I realize that I am not sufficiently familiar with the work on nuclear physics from other points of view to include any adequate discussion of them.

It is well known that nuclear changes occur in atoms, and that many of them are accompanied by emission of radiation, but that radiation does not contribute to such spectra as are observable as the result of ordinary excitation. Some of the nuclear changes apparently are spontaneous; others are traceable to the effects of cosmic rays; still others to bombardment by heavy particles such as protons, deuterium ions, alpha particles or neutrons. Many of these changes require comparatively large amounts of energy to initiate them, and many of them liberate more energy than is required to cause them. Furthermore, these losses or gains in energy are correlated with gains or losses of mass in the sum of the particles observed before and after they occur.

The data derived from observation of such changes as these must be considered in formulating any final scheme of nuclear structure. Study of spectra of unstable isotopes produced by these processes would be of incalculable value, but unfortunately it is not yet possible because the unstable atoms have not yet been produced in sufficient concentrations to permit excitation of their spectra.

Indeed, we know nothing of the spectra that would be produced by single isotopes of any element, if they could be obtained unmixed with other isotopes, except in the case of hydrogen and deuterium. We do know, that the spectra emitted by mixtures of these isotopes of element No. 1 is far more complex than that of either isotope alone. In Chapter 5 I have attributed the complexity of the spectrum of neon — the occurrence of offset series — to the presence of isotopes of sub-element 3. In the case of carbon, very briefly and inadequately discussed in Chapter 6, because data for a better analysis are not yet available, I have suggested that an element may contain isotopes of more than one variety of sub-element, and that forms that are not separable by positive ray analysis may actually be of different composition, though of the same chemical properties, and even may not contain isotopic forms of the same sub-elements.

This probably is true of some of the unstable forms which are produced

artificially in the laboratory, or by nuclear fission. Therefore it is of the utmost importance that as soon as possible the isotopes that may be obtained in comparatively uncontaminated state, whether stable or unstable, should be examined spectroscopically, instead of only chemically and by positive ray analysis. It appears probable * that the isotope C¹⁴ may be available in sufficient purity for spectroscopic examination soon. I predict that its spectrum will be very different from that of ordinary carbon.

If atoms are composed of sub-atoms, as my studies of spectra indicate, accessions or losses of mass of atoms as wholes must be due chiefly to accessions or losses of mass in the sub-atomic nuclei, which may be of different mass numbers though of the same atomic number, or to replacement of one atomic constituent by another as the result of direct impact. If an atom contains several sub-atoms of different atomic number, any one of these may undergo change or be replaced by another, the resulting structure probably being less stable than those of the atoms which normally occur which have endured the vicissitudes of atomic existence for untold ages, under terrestrial conditions. Up to the present time, the results of nuclear changes have been accounted for on the supposition that every atom has a single nucleus. Perhaps considering the probability that the nucleus is complex, as my studies of spectra indicate, may assist, instead of conflict with, the interpretation of artificially produced, unusual isotopes.

Therefore, I will present some suggestions regarding sub-atomic nuclear structure which have occurred to me as a result of study of spectra, with a hope that they may be found helpful not only in the field in which I have been working, but in fields with which I am not familiar, including what is now known as nuclear physics and also to some extent perhaps astronomical physics.

My analysis of the hydrogen spectrum indicates that the force between the hydrogen ion and an electron in the *a* configuration is given by the equation

$$F = \frac{e^2}{r^2} \left(1 - \frac{r_0}{r} \right)$$

and analogy with like spectra of helium and other elements as well as analysis of lines of x-ray spectra suggests the formula

$$F = \frac{e^2}{r^2} \left(N - \frac{r_0}{r} \right)$$

as applicable in like manner to elements of atomic number *N*. From this is easily derived the relationship

$$\frac{dF}{dr} = \frac{N^4 e^2}{r_0^3} = 4\pi^2 \nu^2 m$$

when $r = \frac{r_0}{N}$, ν being the limiting frequency, thus shown to be proportional to N^2 . This formula suffices only for suggestive purposes, for it ignores all

* From a communication published in *Science*, March 7, 1947, from Norris and Snell, of Clinton Laboratories, Oak Ridge, Tenn.

possible configuration of the atom but one, and even then leaves out of consideration the effect of differences in mass.

Ignoring the incompleteness of the formula, we may extrapolate the force exerted upon a hypothetical sub-element of atomic number 0. There would then be a series of sub-elements of increasing atomic number for which the force exerted upon a single external electron, no other electrons being in the vicinity, as given by the following formulas:

$$\begin{aligned} \text{Sub-element 0 } F &= -\frac{e^2 r_0}{r^3} \\ \text{“ 1 } F &= \frac{e^2}{r^2} - \frac{e^2 r_0}{r^3} \\ \text{“ 2 } F &= \frac{2e^2}{r^2} - \frac{e^2 r_0}{r^3} \\ \text{“ 3 } F &= \frac{3e^2}{r^2} - \frac{e^2 r_0}{r^3} \end{aligned}$$

in which $e^2 \left(N - \frac{r_0}{r} \right)$ is the product of two charges.

The energy required to ionize the hydrogen atom from the a configuration as computed in Chapter 8 is $W = \frac{e^2}{2r_0}$. To deprive sub 2 of one electron if it has only one would require four times this energy, but to deprive it of both if it had two poised equally distant from the center would require $W = \frac{35}{16} \frac{e^2}{r_0}$. To remove only one of the two, permitting the other to assume its solitary poised position would therefore require only $\frac{3}{16} \frac{e^2}{r_0}$ of energy, or only $\frac{3}{8}$ as much as to ionize a hydrogen atom in the a configuration. Thus it is seen that in the process of excitation of helium neutral atoms of sub-atom 2 would be very unlikely to occur, and in the liberation of sub 2 from other atoms of higher atomic number they would be more likely to be freed with single electrons accompanying them than with two. Something similar is to be expected of sub-atoms of higher atomic number, and the scheme applied to x-ray spectra in Chapter 7 is in accord with what should be expected from a structure of this type.

In the disintegration of atoms by excitation, however, the a configuration would not be the most likely unless the excitation were severe. Therefore the elaborate enhanced spectra are to be expected instead of the x-ray spectra, if the excitation is moderate.

The hypothetical particle designated sub-element 0 in the schedule and possessing mass number 1 can be identified with the particle of no charge perceptible by passage through ordinary electrostatic or electromagnetic fields known as the *neutron*. It would repel a negative electron which was brought very close to it, and attract a positive electron in its vicinity, though scarcely at all one at an appreciable distance, measured by our ordinary standards.

This neutron would therefore draw into itself a positive electron if one were near, and thus be converted into a hydrogen ion. Let us assume that this did occur, and that another neutron were close at hand. There would still be attraction between the hydrogen ion, which is positive, and the second neutron, which at close range is negative, and the result would be formation of an ion of deuterium, or heavy hydrogen. It is conceivable that a third neutron could be added to the combination, producing an ion of mass number 3.

If, however, it were possible to force into an ion of deuterium an extra positive electron, the result would be an ion of mass number 2 and charge

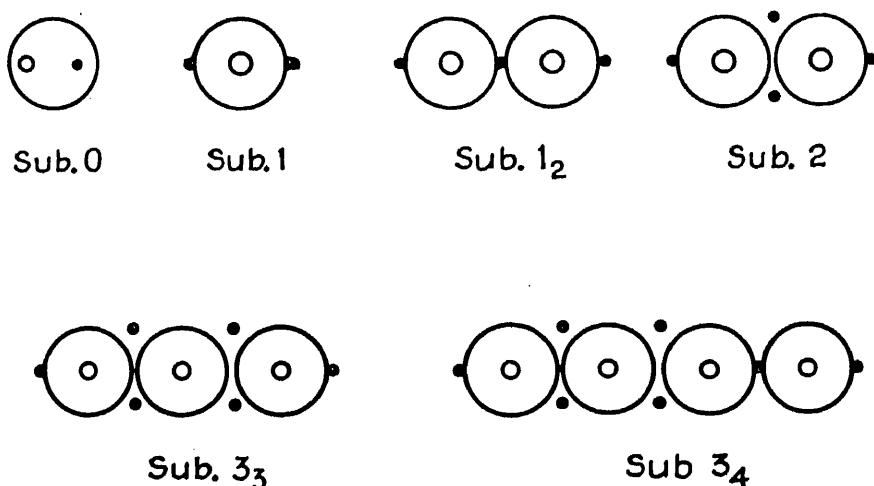


FIGURE 12

$+2e$, which I have designated sub-element 2, which also might be formed by union of two hydrogen ions, if they could be forced close enough together. The scheme can be extended. I have found it helpful to represent the relative positions of positive and negative centers of hypothetical ions of sub-elements 0, 1, 2, and 3 diagrammatically in the accompanying figures, which can account for the existence of two axes to the ions of hydrogen and deuterium, three for the ion of sub 2, which have been found necessary from the analyses in Chapters 2, 3, and 4. The negative centers, but not the positive centers, in all cases are arranged in a straight line if no external electrons are present. If this be extended to sub-atomic nuclei generally, it would account for the Lyman lines of all elements discussed in Chapter 7 as due respectively to two and three such ions of like atomic number in line with two or three negative electrons also in line. The regularity of the progressions of K lines of x-ray spectra seems to indicate that the linear configuration within the sub-atomic nucleus may be general.

In the figures dots represent the centers of positive electrons and the small circles centers of negative charge. No attempt is made to indicate

relative sizes of the nuclei, or the distribution of charge within the ion. The larger circles represent units of mass, of the grosser sort, that is, packing fractions disregarded. Two circles indicate mass number 2, three mass number 3, four mass number 4. In the diagrams for the various isotopes of sub 1 and that of sub 2, all the particles would be in the same plane if no external electrons were present; but in that representing sub 3, one pair of positive centers would not lie in the plane of the diagram, as shown, but in a plane at right angles thereto; and in cases of larger atomic number the arrangement would be more complicated. This must lead to greater complexity of spectra produced with the assistance of sub-atoms of larger atomic number, and particularly of spectra of higher orders of such elements.

If this general scheme of nuclear structure be extended without modification, it would require for sub-atom 82, which is the atomic number of lead, 82 negative centers and 164 positive ones, with a total gross mass number 82. If one neutron were added to one end, the mass number would be 83, and if neutrons were added at both ends it would be 84. The mass numbers of the stable isotopes of lead are 204, 206, 207, and 208. To make up these total masses other sub-atoms enter into the atomic structures, of which it is obvious that there may be several varieties for each stable isotope. Data for the unstable isotopes of lead are not yet announced.

The stability of subatomic nuclei must be due to balance of forces, occasioned by the distribution of charge, and though we do not know what the forces between centers are when the centers are very close together, we do know that when distances are sufficiently large, forces of repulsion as well as those of attraction follow the inverse square law. Therefore the predominance of positive charges in nuclei of large atomic number would increasingly tend to stretch the nucleus when the number of charges in line passed a limit fixed by the nature of the charged particles themselves. Thus there must be a limit to the number of particles in line, and therefore to the maximum atomic number of a stable subatomic nucleus. Moreover, those nuclei that most closely approached that limit would be the ones most likely to be breakable by external influence, especially if not protected by the other sub-atoms which surround them in the chemical atom. A neutron introduced into the nuclear line would weaken it, and it then would be subject to fission, the normal atom of which it was the kernal disintegrating and other atoms, some stable and some unstable, perhaps being reformed from the parts.

There are, however, other means by which a nucleus might be broken. In the case of lead it is known that cosmic rays may produce "showers" of electrons, both positive and negative, the negative ones predominating in number, apparently emitted by a single atom of lead. Either electrons are produced where there were none before, or the cosmic rays, whatever they may be, liberate electrons already in the structure. The latter alternative seems more likely; but since the negative electrons predominate in number, it also seems likely that some, if not most of them come not from the sub-

atomic nuclei, but from the binders which hold the various sub-atoms in the atom closely together.

From such considerations as these it seems to me probable that both the mass and the distributed charge of a sub-atom, and of atoms formed by their aggregation in various configurations, some stable and some very unstable under surrounding conditions, including what may be called "cosmic" ones, are due to the closeness of approach of positive and negative electrons to one another in pairs and in larger groups, and that even the mass of the electron as well as its distributed charge is due to its structure.

What is an electron? How are we to think of it? Some years ago I asked this question of a professor lecturing upon space lattice and his response, after some hesitation, was "I do not think of it at all!" Minds with the same attitude refuse also to think of the "ether" as anything real, or at best regard it as an attribute of space, to be accorded mathematical treatment only. This is by no means a new attitude toward phenomena which we do not understand, and particularly those which we are not able to control. Nevertheless, it is not an attitude that stimulates discovery, and if we hope to conceive of an atom as a structure we must have a physical or at least a pseudophysical model to represent it, and not merely a mathematical formula by which certain unexplained phenomena are partially correlated numerically. If we are to have a model atom we need also a model electron, which is a component part of an atom, separable therefrom, and capable of separate study, at least as to certain of its attributes. To account for light we also must have a model of its mode of propagation; and if light consists of electromagnetic pulses, this implies an ether, a medium capable of accounting for the transmission of those pulses, without involving us in denial of the reality of other phenomena known to us, other than the propagation of light.

Properties of the Ether

There are certain properties of radiation for which our model ether must be able to account, and properties of other kinds which the model must not forbid. Of the ordinary forms of matter with which we are familiar, only gases permit solid bodies to move freely through them without appreciable retardation. In this respect ether must resemble a gas more closely than a solid or a liquid.

If the ether is a gas, it would be expected to circulate approximately with the heavier planets and the sun, at least in their immediate neighborhood, and motion of the earth with respect to it would be small, if at all observable at the earth's surface. This is in keeping with the results of the Michelson-Morley experiment, even if we do not reject the small ether drift Miller believed that he found.

If the ether is a gas it either must be immune to gravitation or its structure and the kinetic motion of its individual particles must on the whole be

so great that the effect of gravitational attraction is negligible, or accountable by those observations now ascribed to relativity.

Since time is required for the transmission of light, the molecules of our model ether must possess inertia; otherwise there would be no reasonable accounting for the comparatively constant velocity of light, at least across the orbit of the earth.

The mean kinetic energy of the ether molecules must be sufficient to maintain it in the gaseous state, under ordinary conditions.

Caution. There is no justification for assuming that the ether is not compressible, as well as capable of transmission of electromagnetic pulses; nor is there any necessity for assuming that the ether pressure and temperature are uniform throughout the visible universe. These are things to be ascertained by observation and analysis, difficult as those may be.

In view of these conditions, the property which enables ether to transmit electromagnetic fields and pulses must reside in the structure of its molecules. I will try to picture a model of a gas that could meet these requirements, qualitatively, leaving the actual dimensions and degrees of the required properties out of the picture. The basic idea is that two particles may be poised with respect to one another, in such a manner that if they are pressed closer to one another there is a force tending to separate them, but if separated a little from the poised position they will be attracted toward one another. This is similar in kind to the idea of the electron poised with respect to the hydrogen ion, forming a neutral molecule of two parts of charge opposite to one another when separated; but in the case of the ether molecule, we must consider the size to be much smaller and the mass much less. One of the ether particles which normally are poised with respect to one another to form a molecule we will call positive, and the other negative; and for the sake of this speculation we will assume that they both have mass and are almost equal but opposite in charge. These molecules must be in rapid motion with respect to one another, as are the molecules of any other gas. The forces between the particles and between the molecules as wholes are assumed to act at a distance, through otherwise empty space. As in Newton's mechanical system, space and time are the only continua assumed, and action at a distance is assumed but not explained to those who find the idea difficult to accept. This model is crude and qualitative only, but it can be thought of consistently.

If, in a limited region of space, there were only a few such molecules, they would tend to line up in elastic chains; but if there were very many and they were agitated by a sufficient amount of motion among themselves, alignment in long chains could not take place. However, let us assume that some collision was so violent that one of these ether molecules was broken into its two parts, and that these were separated from one another a considerable distance in comparison with the mean distance between molecules surrounding them. The ether molecules would then orient themselves, at least partially, about each separated atom, and be drawn closer thereto. In the

case of the positive particle the negative ends of the molecules would point toward the liberated particle, and in the case of the negative particle the direction of orientation would be reversed. Thus positive and negative electrons might be formed, each possessing the sum of the masses of the ether molecules drawn close enough together to be held firmly enough to move substantially with the central particle. The extent to which such accretion could take place would depend upon the mean kinetic energy with which the ether molecules in the vicinity were endowed, the absolute temperature of the surrounding ether, as well as upon the law by which the particles acted upon one another at a distance.

The aggregations which I call electrons would be free to move in the surrounding ether. Although their fields might extend without limit in any region where there is any ether such electron would move as a particle, and could be observed as well as thought of as a *particle*. In this sense only do I regard electrons and ions as discrete. I do not assign to them surfaces or boundaries in the same sense as we think of boundaries or surfaces of solids.

Energy would be required to separate the positive and the negative particles of an ether molecule, and energy would be developed or rather freed by the accretion of ether molecules about each of the separated parts. The difference between these would be released if there were means of again bringing the positive and negative centers together and reforming a molecule of ether. The amount of that energy in any region where the ether temperature and pressure was constant would be the same for all pairs of electrons. If many electrons were reduced to ether the energy liberated would be quantitatively proportional to their number. The mass of electrons would be sub-divided into the masses of the original ether molecules, the total undergoing no change, but there would be a proportionality between the mass of electrons so converted and the amount of energy liberated.

In each electron the ether molecules would be packed closest together near the central particle, but would become less and less close as the distance from the center increased, and the agitation would increase in amplitude and the orientation become less complete as distance from the center increased. The central portion would become more and more "solid" and the outer portion more and more "gaseous" as the distance from the center varied. If we consider such structure possible for an electron our next question is: How can the mass of hydrogen ion, or of a neutron, both of which are more than 1800 times as heavy as an electron, be accounted for?

Let it be supposed that the positive and the negative electron are permitted to approach one another gradually, from a distance apart that must be considered as vast in comparison with the approximate "effective" size of the electrons themselves. The ether molecules between them will tend to orient themselves all directing their axes toward the opposite centers of attraction. In such alignment, which at first will be put partial, owing to the helter-skelter motion of the molecules with respect to one another, the

molecules will attract one another, and be drawn closer together between the central particles. This closeness of packing will be limited by the law of force governing the attractions and repulsions between particles which I have assumed to exist, but which I have not attempted to define mathematically, and also by the amount of kinetic energy in the ether molecules surrounding the assembly. Let us term the resulting body a "free" neutron. Because of the resistance to compression of the aligned or partially aligned particles there will be a definite limit to the mass included in the particle formed by this combination, and a resistance to closer approach of the central particles of the positive and negative electrons respectively. It is conceivable, however, that approach might be so rapid as to break through this protective alignment and permit the central parts of the respective electrons to come together and to form an ether molecule, in which case there must be a release of all of the ether molecules. This would be a genuine explosion within the ether — an expansion of the ether under pressure occasioned originally by the separation of individual particles and the attractions of the molecules in the surrounding medium consequent upon it.

If the neutron is formed in this way, there must be locked up within it somewhat more than 1800 times as many ether molecules as in either a positive or a negative electron alone.

According to the same scheme, the mass of the hydrogen ion must be explicable as due to a combination of one negative electron and two positive electrons. The positive electrons tend to repel each other, and the packing to be expected would not be as close as in the neutron, and the mass of the resulting ion would certainly not be double that of the neutron. Practically, we know that the masses are very nearly the same, the present opinion of those working in this field experimentally as well as theoretically being that the mass of the "free" neutron is a little greater than the mass of the hydrogen atomic ion. Accurate determinations of the masses of these particles and of the electrons, both positive and negative, may eventually afford some data by which this scheme may be represented quantitatively, and something about the properties of the individual ether molecule and of its parts may be given mathematical representation.

The scheme may be amplified to account for sub-atoms of larger atomic number and their isotopes, and it seems to me to be capable eventually of accounting for packing fractions to a first approximation. If it is sound in principle, there must also be variations in the quantity of ether included within the structures of atoms by the union of different sub-atoms, although the variations in mass due to such cause must be very much less than in the formation of the sub-atomic nuclei. Furthermore, there is to be expected very much less variation in mass due to the combinations of chemical atoms with one another. From this point of view the Einstein equation expressing equivalence of mass and energy, or something akin to it, may be found justified without assuming any change in the inertia of the "ultimate" particles of which matter is composed, but only in the number of

them locked up by compression in the ordinary forms of matter with which we now are able to deal.

This brings us to consideration of the question: What change in mass of an electron, if any, is occasioned by its motion with respect to its surroundings, which means with respect to the surrounding ether by accretions from which its mass is derived? Einstein relativity theory asserts that the mass of any body is increased by its velocity with respect to surrounding bodies, or to "the observer" according to the formula

$$m = m_0 \frac{1}{\sqrt{1 - \frac{v^2}{c^2}}}$$

in which m_0 is the mass of the body at rest, m its mass in motion with the velocity v , and c the velocity of light. This formula is not based upon study of the electron, but upon other phenomena interpreted by relativity theory; but the behavior of the electron when moving very rapidly in electrical or magnetic fields is supposed to confirm it. I do not propose to discuss the applicability of this formula to the motions of the planets or the legitimacy of the relativity theory generally, but only its applicability to the electron, which is a very special kind of body, which always manifests charge as well as mass. Interpretation of the motions of the electrons that are supposed to confirm the Einstein equation assume that the charge of the electron is an absolute constant, independent of velocity, and that mass only is altered as the velocity increases.

What actually is observed by experiment is not a change in either mass or charge, but a change in the ratio of mass to charge, the ratio e/m , as determined by Thomson's method or a similar one. Assuming the interpretation of Thomson to be correct, the relationship observed is

$$\frac{e}{m} = \frac{e_0}{m_0} \sqrt{1 - \frac{v^2}{c^2}} \quad \text{or} \quad \frac{m_0}{m} = \frac{c_0}{c} \sqrt{1 - \frac{v^2}{c^2}}$$

in which either e or m or both may be variable, so far as the observations themselves disclose. This gives us

$$m = m_0 \frac{e}{e_0} \frac{1}{\sqrt{1 - \frac{v^2}{c^2}}}$$

and not

$$m = m_0 \frac{1}{\sqrt{1 - \frac{v^2}{c^2}}}$$

which is true only if e is invariable. From the structure of the electron assumed in the foregoing discussion it seems more likely that e may be more variable than m , or that both e and m vary with velocity of the electron through the surrounding ether.

The kinetic energy of the moving electron therefore would be

$$W = \frac{mv^2}{2} = \frac{m_0 v^2}{2} \frac{e}{e_0 \sqrt{1 - \frac{v^2}{c^2}}}$$

which would become infinite if $v = c$ only if e could not become zero at the velocity of light. For illustration we may assume several cases, first that m is constant. Then the kinetic energy is $\frac{m_0 v^2}{2}$ and the "effective" charge is $e = e_0 \sqrt{1 - \frac{v^2}{c^2}}$ for any value of v .

Next assume that $e = e_0 \sqrt{1 - \frac{v}{c}}$. Then $m = \frac{m_0}{\sqrt{1 + \frac{v}{c}}}$ and $W = \frac{m_0 v^2}{\sqrt{1 + \frac{v}{c}}}$

Then at the velocity of light $e = 0$ and $m = m_0 \div \sqrt{2}$. If m diminishes more rapidly than indicated in the above schedule, e also must diminish more rapidly, and the energy at any velocity will be less than in the schedule.

These illustrations are suggestive only, as the law of variations of e with v is not known from observation. It may be hoped, however, that at some future time this law may be supplied by experiments not hitherto made. Because of its far greater mass a positive ion would not be accelerated as much by a given voltage as an electron, and its charge and mass would be less affected by the velocity imparted by a specified voltage. Consequently the kinetic energy of a positive ion might be much nearer to the product of the rest charge into the voltage when the voltage is high than would be the case with our model electron. This is in keeping with the fact that in Wilson cloud chambers the paths of alpha particles are longer than those of the fastest electrons and the amount of ionization produced by alpha particles and other positive ions much greater than by electrons accelerated by like voltages.

Those interested in studying the relationship between the mass of the electron and its velocity from a different point of view may be referred to the discussion of Mr. C. A. Boddie, of Alexandria, Virginia in a paper entitled "The Motional Mass of the Electron" printed in January 1947 issue of *Electrical Engineering*.

Since the days of Huygens and Newton there has been difficulty in reconciling the facts known about gravitation with the facts known about light. This difficulty originally consisted at least in large part in reconciling the existence of a medium possessing mass with gravitational theory. That difficulty still remains, and there has been added to it a difficulty in accounting for two kinds of forces acting at a distance, the gravitational forces and the electrical forces. There is a confusion of thought, due to the proportionality of gravitational attraction and mass as inertia — the mass which resists acceleration — a confusion which might disappear if gravitation could be shown to be a residual electrical attraction.

During my attempts to account for spectra in a consistent manner, not antagonistic to electromagnetic theory, a scheme for deriving gravitational from electrical forces has occurred to me which I venture to include among the speculations of this chapter, although I know that it is not provable

from the data of spectroscopy with which this book is concerned. It has interested me, and it may interest others, though perhaps only as a curiosity.

The forces between charged particles such as I have been discussing in this chapter cannot take place along straight lines, like a pull exerted by a string. The "lines of force," to use the term of Faraday, are curves, whether they occur in a gaseous medium as I have assumed for the purpose of developing a model, or in some other medium which I have been unable to conceive. At the origin, or end, they radiate, in the system I have described, from positive and negative electrons. The fields, therefore, cannot be fully and correctly expressed mathematically by a single real force, but must be capable of more complete mathematical expression as a combination of a real term and an imaginary term, using the word imaginary in its mathematical sense only, which involves the concept of direction.

Let us therefore represent the charge of a positive electron as the sum of a real term of magnitude a and of an imaginary term of magnitude x and the charge of a negative electron by a real term b plus an imaginary term y . The charge of a neutron would then be $(a - b) + \sqrt{-1} (x - y)$ and the attraction or repulsion between two such neutrons would be the square of this sum divided by the square of the distance between the neutrons, provided they were far apart in comparison with atomic dimensions. This product is

$$(a - b)^2 + 2\sqrt{-1}(a - b)(x - y) - (x - y)^2$$

in which the middle term is imaginary and cannot be either attraction or repulsion. The real term will be positive, and the force repulsion, if $a - b$ is greater than $x - y$, and it will be attraction if $x - y$ is slightly greater than $a - b$. It is possible that this slight difference may be evaluated in a manner which will account numerically for the gravitational constant.

TABLES OF DATA

Table 1. (Part I)

LEVELS		O-O Nulls of the principal band systems, as due to differences between "levels" joined by vertical lines. For band structure see the tables of which the numbers are given at the top of each vertical line indicating the nulls.
Symbol	Wave Nos.	
b	117754.43	23 - 21621.84
a	109678.	24 - 23188.83
ba	35375.27	25 - 33000.00
bb	29326.52	26 - 22667.76
aa	27419.50	27 - 16612.39
ab		28 - 26232.57
bba	19074.51	29 - 27289.62
aba	18762.94	30 - 27469.71
bbb	12988.66	31 - 42895.74
abb	12707.51	32 - 24847.54
baa	12435.10	33 - 24768.28
aaa	12186.44	34 - 22234.83
bab	6365.08	35 - 22277.31
aab	6157.58	36 - 17140.08
bbaa	13753.44	37 - 16891.42
abaa	13451.93	38 - 16619.01
bbab	13716.57	39 - 20564.62
abab	13425.35	40 - 15233.06
bbba	7325.70	41 - 11736.49
abba	7055.21	42 - 98991.55
bbbb	7273.20	43 - 90334.93
abbb	7013.36	44 - 106631.09
baaa	7091.69	45 - 105290.88
aaaa	6854.87	46 - 102828.13
baab	7057.99	47 - 97491.56
aaab	6834.66	48 - 82258.50
baba	644.34	49 - 36 - 12709.43
aaba	449.08	50 - 41 - 41
babb	603.38	51 - 13335.50
aabb	417.94	52 - 6480.24
bbbaa	11229.10	53 - 2308.82
abbaa	11143.11	54 - 2524.34
aabba	4478.98	
bbaaa	4530.04	
baaaa	4430.78	
aaaaa	4387.12	
aaaab	4369.27	
bbaba	1856.81	
baabb	2036.90	
aabbaa	3093.95	
aaaaaa	3046.61	

Allocation of the difference numbers 2524.34, 2308.82, and 4162.1 may require correction when Part II of Table 1 has been extended and corrected to include all levels assignable to line molecules with five atoms in line.

TABLES OF DATA

Table 1. (Part II)

Levels			Wave Number Differences between Levels Having the Same Value of n						
n	Symbol	Wave No.	Col. 1	Col. 2	Col. 3	Col. 4	Col. 5	Col. 6	Col. 7
1	<i>b</i>	117754.43							
1	<i>a</i>	100678.	<u>8076.43</u>						
2	<i>ba</i>	35375.27							
2	<i>bb</i>	29326.52	<u>6048.75</u>						
2	<i>aa</i>	27419.50	<u>1907.02</u>	<u>7955.77</u>					
2	<i>ab</i>								
3	<i>bba</i>	19074.51							
3	<i>aba</i>	18762.94	<u>311.87</u>						
3	<i>bbb</i>	12988.66		<u>6085.85</u>					
3	<i>abb</i>	12707.51	<u>281.15</u>	<u>6055.43</u>	<u>6307.00</u>				
3	<i>baa</i>	12435.10		<u>553.56</u>	<u>6327.84</u>	<u>6030.41</u>			
3	<i>aaa</i>	12186.44	<u>248.86</u>	<u>521.07</u>	<u>802.22</u>	<u>6576.50</u>	<u>6887.07</u>		
3	<i>bab</i>	6365.08		<u>6070.02</u>	<u>6342.43</u>	<u>6623.68</u>	<u>12397.86</u>	<u>12700.43</u>	
3	<i>aab</i>	6157.58	<u>207.50</u>	<u>6018.86</u>	<u>6277.52</u>	<u>6549.93</u>	<u>6831.08</u>	<u>12605.36</u>	<u>12016.03</u>
4	<i>bbaa</i>	13753.44							
4	<i>abaa</i>	13451.93	<u>- 301.51</u>						
4	<i>bbab</i>	13716.57	<u>+ 264.04</u>	<u>36.87</u>					
4	<i>abab</i>	13425.35	<u>- 201.22</u>	<u>26.58</u>	<u>328.09</u>				
4	<i>bbba</i>	7325.70							
4	<i>abba</i>	7055.21	<u>- 270.49</u>						
4	<i>bbbb</i>	7273.20	<u>+ 217.00</u>	<u>52.50</u>					
4	<i>abbb</i>	7013.36	<u>259.84</u>	<u>41.85</u>	<u>312.34</u>				
4	<i>baaa</i>	7091.09	<u>+ 78.33</u>	<u>- 182.51</u>	<u>+ 36.48</u>	<u>- 234.01</u>			
4	<i>aaaa</i>	6854.87	<u>- 230.82</u>	<u>- 158.49</u>	<u>- 418.93</u>	<u>- 200.34</u>	<u>- 470.83</u>		
4	<i>baab</i>	7057.99	<u>+ 203.12</u>	<u>33.70</u>	<u>+ 44.83</u>	<u>- 215.21</u>	<u>+ 2.78</u>	<u>- 207.71</u>	
4	<i>aaab</i>	6834.66	<u>223.32</u>	<u>20.21</u>	<u>257.03</u>	<u>- 178.70</u>	<u>- 448.54</u>	<u>- 220.55</u>	<u>- 480.04</u>
4	<i>baba</i>	644.34							
4	<i>aaba</i>	440.08	<u>105.26</u>						
4	<i>babb</i>	603.38		<u>40.96</u>					
4	<i>aabb</i>	417.04	<u>185.44</u>	<u>31.14</u>	<u>226.4</u>				

The differences derived from analysis of hydrogen bands in Tables 2 to 47 are underscored. To include all differences for pairs for which $n = 4$ would require fifteen columns. Some such differences may prove significant, but not necessary for the present purpose.

Table 1. (Part III)

Hydrogen Levels Attributable to Line Molecules with Five Atoms in Line

Mol.	Wave No.	Differences				
<i>bbbaa</i>	11110.53					
<i>bbbab</i>	11082.83	33.70				
<i>abbaa</i>	11027.70		88.83			
<i>abbab</i>	10905.10	32.00		87.73		
<i>babaa</i>	10979.09				130.54	
<i>babab</i>	10962.40	17.50			120.43	
<i>aabaa</i>	10893.35				134.45	223.18
<i>aabab</i>	10877.53	15.82			117.57	205.30
						239.00
<i>bbbb</i>	4070.60					
<i>bbbbb</i>	4018.57	52.12				
<i>abbb</i>	4011.13		59.56			
<i>abbbb</i>	4504.41	46.72		54.16		
<i>babba</i>	4534.05				136.04	
<i>babb</i>	4480.23	45.42			120.34	
<i>aabba</i>	4478.03			55.07	132.20	101.76
<i>aahbb</i>	4437.10	41.88		52.13		181.47
						234.59
<i>bbnaa</i>	4500.86					
<i>bbnab</i>	4528.03	31.03				
<i>abnaa</i>	4502.68			58.28		
<i>abaab</i>	4470.54	32.04		58.39		
<i>buaaa</i>	4440.07				114.79	
<i>buaab</i>	4425.16	20.01			103.77	
<i>aaaaa</i>	4387.12			58.95	115.46	173.74
<i>aaaaab</i>	4307.78	10.34		57.38		161.15
						193.08
<i>bbaba</i>	— 1701.03					
<i>bbabb</i>	— 1760.15	58.22				
<i>ababa</i>	— 1748.06			44.13		
<i>ababb</i>	— 1701.01	44.05		30.86		
<i>baaba</i>	— 1836.00				134.73	
<i>baabb</i>	— 1863.35	26.00			103.20	
<i>aaaba</i>	— 1883.71			47.05	137.65	181.78
<i>aaabb</i>	— 1800.05	13.24		33.00		136.80
						195.02

This part was revised September 30, 1947, after other tables were in type. Revision and corrections were assisted by interpretation of multiplet differences of second order spectra of Na, K, Rb, Cs and Kr. The following corrections of allocation of difference numbers should be made on Part I.

$$2524.34 = abbb-babbb$$

$$2308.82 = abab-bbbba$$

$$4162.1 = abbba-aaba$$

Table 1. (Part IV)

LEVELS		Significant Differences found by Band Analysis between Levels for which n = 3 and Levels for which n = 4.
Symbol	Wave No.	
bba	19074.51	
aba	18762.94	
bbb	12988.66	
abb	12707.51	
baa	12435.10	
aaa	12186.44	
bab	6365.08	
aab	6157.58	
bbaa	13753.44	
abaa	13451.93	
bbab	13717.57	
abab	13425.35	
bbba	7325.70	
abba	7055.21	
bbbb	7273.20	
abbb	7013.26	
baaa	7091.69	
aaaa	6854.87	
baab	7057.99	
aaab	6834.66	
		697.29
		900.41
		934.11
		855.78
		1168.12
		725.61
		648.28
		908.12
		5094.75
		1567.00
		990.25
		744.42
		1318.34
		1045.93
		7764.78

Table 2. Calculated Lines and Levels of the Primary Spectrum Assuming $N = 109678$

	Levels	Lines					
		$N + n^2$	Lyman $N\left(1 - \frac{1}{n^2}\right)$	Balmer $N\left(\frac{1}{2^2} - \frac{1}{n^2}\right)$	Paschen $N\left(\frac{1}{3^2} - \frac{1}{n^2}\right)$	$N\left(\frac{1}{4^2} - \frac{1}{n^2}\right)$	$N\left(\frac{1}{5^2} - \frac{1}{n^2}\right)$
1a	109678.00						
2a	27419.50	82258.50					
3a	12186.44	97491.56	15233.06				
4a	6854.87	102828.13	20504.02	5331.56			
5a	4887.12	105290.88	23032.28	7709.31	2407.75		
6a	3046.01	106031.39	24302.89	9130.82	3808.28	1340.51	
7a	2238.33	107439.07	25181.17	9948.12	4616.54	2148.79	808.28
	Limit	109678.00	27419.50	12186.44	6854.87	4887.12	3046.01

Table 3. The Principal Series of the Alpha Band System

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Venable: $bb-abb = 16619.01$

Wave numbers and intensities by Gale. Classification by Richardson. Nulls, differences and levels by Venable. First, second and third differences show regularities and irregularities in progressions.

Branch R			Branch Q									
Differences			Lines	I	n	Differences			Lines	I	n	Band
			16019.01						16019.01			0,0
			16078.57	10	0				16011.43	10	1	
	- 7.58	+ 50.50	10730.55	10	1	+ .10	- 7.48	- 7.68	16506.37	10	2	
- .55	- 8.11	+ 43.87	10774.42	0	2	+ .11	- 7.37	- 15.00	16573.04	10	3	
- .48	- 8.50	+ 35.28	10800.70	0	3	+ .17	- 7.20	- 22.43	16544.31	2	4	
- .35	- 8.04	+ 26.34	10836.04	1	4	+ .23	- 6.07	- 29.03	16507.71	2	5	
- .43	- 0.37	+ 10.07	10853.01	1	5	+ .25	- 6.02	- 36.00	16404.40	0	6	
- .47	- 0.84	+ 7.13	10860.14	1	6	+ .18	- 6.44	- 43.22	16414.83	0	7	
- .52	- 10.30	- 3.23	10856.91	1	7			- 49.00				
			16337.00						16337.00			1,1
			16303.70	9	0				16330.50	10	1	
	- 8.78	+ 55.80	16440.72	10	1	+ .08	- 7.23	- 7.31	16316.05	6	2	
- 2.80	- 11.04	+ 35.38	16476.10	7	2	+ .09	- 7.14	- 14.54	16204.37	10	3	
+ 1.83	- 9.81	+ 25.57	16501.07	00	3	+ .20	- 0.94	- 21.08	16205.75	3	4	
						+ .22	- 0.72	- 28.02	16230.41	2	5	
						+ .85	- 7.57	- 35.34	16187.50	1	6	
								- 42.91				
			16067.36						16067.36			2,2
			16121.52	5	0				16060.31	10	1	
	- .73	- 6.73	16168.05	10	1	+ .07	- 0.98	- 7.05	16040.28	7	2	
- .02	- 7.46	+ 39.07	16208.02	4	2	+ .09	- 0.80	- 14.03	16025.30	10	3	
- .75	- 8.08	+ 31.89	16240.81	5	3	+ .28	- 0.71	- 20.92	16007.73	2	4	
- .50	- 8.83	+ 23.06	16263.87	1	4	+ .24	- 0.47	- 27.03	16003.03	2	5	
	- 0.53	+ 13.53	16277.40	1	5			- 34.10				
			15807.57						15807.57			3,3
			15859.80	5	0				15800.76	10	1	
- 2.38	- 5.02	+ 52.20	15905.53	10	1	+ .10	- 0.71	- 0.81	15787.23	7	2	
+ .78	- 8.00	+ 45.67	15943.20	3	2	+ .11	- 0.60	- 13.52	15767.10	7	3	
	- 7.22	+ 30.45	15973.05	r d	3	+ .12	- 0.48	- 20.13	15740.49	1	4	
						+ .13	- 0.35	- 26.61	15707.53	1	5	
								- 32.00				

Table 3 (Cont'd)

Branch Q (Cont'd)					Branch P						
Differences		Lines	I	n	Band No.	Differences		Lines	I	n	Band No.
- 6.45	- 6.54	15558.91			4-4			16479.00	7	2	0-0
	- 12.99	15552.37	10	1		- 79.27		16399.70	10	3	
	- 19.33	15539.38	3	2		- 5.53	- 84.80	16314.99	4	4	
	- 6.34	15520.05	3	3		- 5.13	- 89.03	16226.00	8	5	
	- 6.07	15494.65	0	4		- 4.06	- 94.59	10180.47	2	6	
	- 6.13	15463.12		5		- 3.89	- 98.70	10031.77	2	7	
		15322.09						16203.95	7	2	
	- 6.18	15315.91	3	1			- 77.76	16126.19	10	3	
	- 12.29	15303.52	1	2		- 9.27	- 87.01	16039.18	5	4	
	- 6.12	15285.11	2	3		- 5.96	- 92.97	15946.21	r	5	
- 5.85	- 5.02	15098.76			6-6			15941.22	5	2	2-2
	- 11.77	15002.84	2	1		- 71.12		15870.10	10	3	
	- 11.62	15081.07	0a	2		- 5.00	- 76.21	15793.99	5	4	
		15063.45	0h	3		- 4.90	- 81.10	15712.79	6	5	
		14885.15	1a	1		- 4.75	- 85.85	15626.94	1	6	
								15688.81	5	2	
		14696.13	0	1		- 6.85		15621.96	10	3	
						- 5.64	- 72.49	15549.47	3	4	
						- 3.55	- 76.04	15473.43		5	

Progressions of Nulls

	29326.52		bb
	12707.51		abb
0,0	10610.01		bbb-abb
1,1	16337.90	281.11	bbb-abbb
2,2	16067.36	270.54	bbbb-abba
3,3	15807.57	250.79	bbbb-abbb
4,4	15558.91	248.66	baaa-aaa
5,5	15322.00	236.82	baaa-aaaa
6,6	14098.76	223.33	baab-aaab
7,7			
8,8			

The "horizontal" difference system of Tables 4 and 5 combines with this system, producing a total of 232 lines classified by Richardson.

Table 4. Q Branches of Alpha Band System Classified by Richardson.
(Some lines omitted to shorten table.)

Wave No.	Diff.	Wave No.	Diff.	Wave No.	Diff.	Wave No.	Diff.	Wave No.
						Band 0-0		Band 0-1
						18611.43	2521.43	14000.4
						18690.37	2514.57	14081.8
						18673.94	2504.84	14069.1
						18544.31	2491.91	14052.4
						18507.71		
						18404.40		
				Band 1-0		Band 1-1		Band 1-2
				18851.06	2521.07	18330.50	2385.00	13945.5
				18830.58	2514.53	18316.05	2378.85	13937.2
				18790.23	2504.80	18294.37	2369.37	13925.0
				18757.83	2402.08	18265.75		
				18708.54	2476.13	18230.41		
				Band 2-0	Band 2-1	Band 2-2		Band 2-3
				20006.52	2385.13	18445.44	2253.01	13807.3
				20039.70	2514.70	18425.06	2240.85	13799.4
				20890.62	2504.85	18304.77	2237.07	13787.6
						18354.75	2225.03	13772.1
						18305.25	2210.43	13753.2
Band 3-0		Band 3-1		Band 3-2		Band 3-3		Band 3-4
22900.00	2521.11	20438.80	2385.00	18053.80	2253.04	15800.70	2123.76	13677.0
22027.58	2514.00	20412.06	2378.83	18034.15	2240.92	15787.23	2117.73	13669.5
		20374.20	2360.45	18004.84	2237.74	15707.10	2108.80	13658.3
		20323.15	2357.00	17906.00	2225.57	15740.49		
		20250.51	2341.03	17917.88	2210.35	15707.53		
Band 4-1		Band 4-2		Band 4-3		Band 4-4		Band 4-5
22314.40	2385.18	19020.31	2253.08	17676.23	2123.56	15552.37	1906.57	13555.8
		19004.16	2240.02	17657.24	2117.86	15530.35	1900.58	13548.8
		10866.70	2237.80	17628.00	2108.85	15520.85	1981.75	13538.3
				17591.22	2090.57	15404.05		
				17545.14	2082.02	15403.12		
Band 5-2		Band 5-3		Band 5-4		Band 5-5		Band 5-6
21080.41	2253.05	19436.36	2123.86	17312.48	1096.57	15315.01	1800.81	13446.1
		19411.80	2117.70	17294.13	1990.61	15303.52	1864.02	13439.5
				17206.82	1981.79	15285.11	1854.01	13430.2
Band 6-3		Band 6-4		Band 6-5		Band 6-6		Band 6-7
21033.10	2123.10	18050.10	1096.50	16902.03	1800.79	15002.84	1742.24	13350.6
21053.12	2117.02	18035.50	1900.50	16944.04	1803.87	15181.07		
21009.39	2100.14	18900.25	1081.70	16918.46	1855.01	15063.45	1730.05	13335.4
Band 7-4		Band 7-5		Band 7-6		Band 7-7		Band 7-8
20403.05	1000.80	18407.14	1800.85	10027.29	1742.14	14885.15	1611.65	13273.5
Band 8-5		Band 8-6		Band 8-7		Band 8-8		Band 8-9
19010.73	1800.81	18040.02	1742.16	17307.76	1011.03	14096.13		

TABLES OF DATA

Table 4 (*Cont'd.*). *R* Branches of Alpha Band System Classified by Richardson, Showing "Horizontal Differences," as Given in "Molecules Hydrogen and Its Spectrum," page 168

	Line	Diff.	Line	Diff.	Line	Diff.	Line
Band					0-0 18678.57 18730.55 18774.42 18808.70 18836.04 18853.01 18880.14 18886.01	2524.17 2521.05 2514.62 2504.84	0-1 14154.4 14200.5 14259.8 14304.86
Band			1-0 18918.02 18981.78 18990.07 19006.46	2524.32 2521.06 2514.57 2504.79	18939.70 18440.72 18476.10 18505.67	2388.30 2385.12 2378.80	1-2 14005.4 14055.6 14087.3
Band	2-0 21034.17 21075.22 21102.54 21114.89	2524.39 2521.17 2514.77 2504.65	18509.78 18554.05 18587.77 18610.24 18620.88 18618.04	2388.26 2385.10 2378.85 2368.48 2356.99 2341.54	16121.52 16168.05 16208.92 16240.81 16263.87 16277.40	2256.12 2251.05 2246.82 2237.71 2225.67 2210.60	2-3 13865.4 13915.0 13962.1 14003.1 14038.2 14066.3
Band			3-2 18115.94 18158.55 18190.12 18211.64	2256.08 2253.02 2246.92 2237.99	15859.86 15905.53 15943.20 15973.65	2126.86 2123.93 2117.80	3-4 13733.0 13781.6 13825.4

The principal series of this system is in the order 0-0, 1-1, 2-2, 3-3, as arranged above. This *R* series terminates with the 3-3 band. The *Q* series (see Sheet 1) are longer. For vertical differences, see Table 3.

Table 4 (*Cont'd.*). *P* Branches of Alpha Band System Classified by Richardson, "Molecular Hydrogen," page 170.

	Line	Diff.	Line	Diff.	Line	Diff.	Line
Band					0-0 16479.06 16399.79 16314.90 16225.06 16130.47 16031.77	2514.56 2504.79	0-1 13904.5 13895.0
Band			1-0 18718.52 18831.03 18831.23	2514.59 2504.84 2492.05	16203.93 16126.19 16039.18 15946.21	2378.73 2369.39 2356.88	1-2 13825.2 13756.8 13682.3
Band	2-0 20744.45 20530.45	2504.94 2476.09	18320.06 18239.51 18150.57 18054.39 17949.95	2378.84 2369.41 2356.08 2341.60 2323.01	15941.22 15870.10 15793.89 15712.79 15626.94	2246.92 2237.70 2225.49 2210.59	2-3 13694.3 1363.24 13508.4 13502.2
Band	3-1 20314.59 20229.13	2378.86 2369.39	17935.73 17859.74 17775.06	2246.92 2237.78 2225.59	15688.81 15621.96 15549.47 15473.43	2117.81 2108.86 2006.77	3-4 13671.0 13513.1 13452.7

Note that the initial horizontal difference number in Sheet 1 is 2524.17, in Sheet 2 is 2521.03, in Sheet 3 is 2514.56. The same horizontal number systems apply to all three branches.

This horizontal number system is analyzed in Table 5.

Table 5

Horizontal Difference System Beginning with 2524.34

0-1			1-2			2-3			2-4		
2524.34			2388.30			2256.10			2126.76		
2521.07	3.27		2385.13	3.17		2253.04	3.06		2123.86	2.80	
2514.53	0.54	3.27	2378.78	6.35	3.18	2246.92	6.12	3.06	2117.86	6.00	3.20
2501.80	9.07	3.13	2369.41	9.37	3.02	2237.74	9.18	3.06	2108.85	9.01	3.01
2492.08	12.78	3.11	2357.02	12.39	3.02	2225.57	12.17	2.99	2096.57	12.28	3.27
2476.13	15.05	3.17	2341.82	15.40	3.01	2210.35	15.22	3.05	2082.02	15.45	3.17
4-5			5-6			6-7					
1000.45			1872.75			1744.98					
1000.57	2.85		1869.79	2.96		1742.18	2.80				
1000.61	5.06	2.88	1863.87	5.82	2.86						
1081.71	8.00	2.94	1855.01	8.76	2.94						
						Nulls Differences					
						2524.34			bbaa-bbbaa		
						2388.30	136.04		bbbbba-babba		
						2256.10	132.20		abba-aabba		
						2126.76	129.34		bbbbbabbbb		
						1000.45	127.31		abbbb-abbbb		
						1872.75	126.70				
						1744.98	127.77				

These differences combine with the systems of which the principal series are given in Tables 3, 11, 17, 18, 35 and 43.

The allocation of 2524.34 may require revision.

Table 6

Horizontal Difference System Beginning with 1318.34

0-1			1-2			2-3			3-4		
1318.34			1281.47			1246.71			1213.01		
1310.41	1.03		1279.84	1.03		1245.25	1.46		1211.76	1.25	
1312.55	3.80	1.03	1270.00	3.24	1.61	1242.38	2.86	1.40	1200.07	2.89	1.44
1300.94	5.71	1.85	1271.81	4.78	1.54	1238.12	4.25	1.39	1205.07	3.90	1.21
1299.08	7.20	1.55	1205.50	0.22	1.44	1232.61	5.51	1.26	1200.10	5.07	1.17
1290.99	8.69	1.43	1258.04	7.55	1.33	1225.89	6.72	1.21	1193.86	6.24	1.17
1280.94	10.05	1.36	1240.32	8.72	1.17	1218.02	7.80	1.14	1186.75	7.11	.87
4-5			5-6			6-7					
1170.95			1147.50			1115.5					
1178.77	1.18		1146.32	1.18		1114.32	1.18				
1170.33	2.44	1.26	1144.00	2.32	1.14	1112.0	2.28	1.10			
1172.74	3.50	1.15	1140.04	3.36	1.04	1108.7	3.3	1.02			
1168.03	4.71	1.12	1136.15	4.40	1.13	1104.3	4.4	1.1			
1162.25	5.78	1.07	1130.77	5.35	.89	1099.0	5.3	.9			
1155.5	6.75	.97	1124.8	5.07	.59	1092.6	6.4	1.1			
						Nulls Differences					
						1318.34			bbaa-baa		
						1281.47	30.87		bbaa-bbab		
						1240.71	34.76		bbbab-bbbbab		
						1213.01	33.70		baba-baab		
						1170.95	33.06		abbba-abbab		
						1147.50	32.45		bbaaa-bbnab		
						1115.5	32.		abaaa-abaab		

These differences combine with the principal series given in Tables 9, 12, 23 to 33, 41, 42 and 44 to 47. Allocation of these differences is provisional.

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Table 7

Horizontal Difference System Beginning with 2308.82

0-1			1-2			2-3		
2308.82			2174.37			2037.79		
2305.50	3.27		2171.38	2.99		2040.25	+ 2.46	
2299.21	6.38	3.21	2165.40	5.98	2.99	2045.18	+ 4.03	+ 2.57
2289.56	0.05	3.27	2156.21	9.19	3.21	2025.18	20.00	- 20.00
2277.48	12.13	2.48	2144.07	12.14	2.95			
2261.08	15.45	3.32	2128.95	15.12	2.98			
2243.51	18.47	3.02	2111.01	17.84	2.72			
2222.06	20.85	2.38	2000.54	20.47	2.82			
Alternates								
2289.56	9.65		2171.38	2.99				
2274.14	15.42	5.77	2163.88	7.80	4.81			
2257.67	18.47	1.05	2146.92	16.66	8.86			
			2165.09	+ 18.17				
Nulls								
			Differences					
			2308.82			<i>abaa-abba</i>		
			2174.37	134.45				
			2037.79	136.54				

This system combines with the systems of which the principal series are given in Tables 14 and 36 to 40. Allocation of 2308.82 is provisional only.

Table 8. Raman Differences in Hydrogen (Rosetti)

0-0 Band

4162.1 <i>bbaaa-aabb</i>	<i>bbaaa</i> 4580.04 (Table 1)
4156.0 - 6.1	<i>aabb</i> 417.94
4144.8 - 11.2 - 5.1	4162.1
4126.9 - 17.9 - 6.7	

Origin and Structure Venable	Rosetti Wave No. Group	
<i>bbb-abb</i>	$3560.32 - .42 = 3568.9$ $+ 281.15 \quad \quad \quad 238.5$	3-1
<i>bba-aba</i>	$3850.47 - 43.07 = 3807.4$ <u>311.63</u> $\quad \quad \quad 354.7$	2-0
<i>bbaaa-aabb</i>	$4162.10 \quad = 4162.1$	0-0
<i>bba-aba</i>	<u>311.63</u> $\quad \quad \quad 336.3$	
<i>aaaa-aaab</i>	$4473.73 + 24.27 = 4498.4$ <u>223.32</u> $\quad \quad \quad 215.3$	0-2
<i>bab-aab</i>	$4697.05 + 16.65 = 4713.7$ <u>207.50</u> $\quad \quad \quad 204.1$	1-3
<i>baba-aaaba</i>	$4904.55 + 13.25 = 4917.8$ <u>195.26</u> $\quad \quad \quad 192.0$	2-4
	$5099.81 + 9.00 = 5109.8$	3-5

The above schedule is provisional. The smaller differences, 43.07, 24.27, 16.65, 13.25 and 9.00 have not yet been allocated in Table 1, but occur in band structure of various bands as set forth in other tables.

Allocation of 4162.1 is provisional.

Table 9. B-A Absorption Bands

d_s	d_1	Lines	I		d_s	d_1	Lines	I	
- 60	- 138	90197	2	Null 0-0	- 104	- 240	98301	1	Null 7-0
	- 96	90336			+ 24	- 136	541	3	
	- 230	0			- 160	677	3		
	- 156	083	2				98837		
	- 199	89832	2			- 98	739	3	
	- 136	91517	3			- 42	500	3	
	- 97	91653				- 64	395	1	
	- 556	556	3			- 82	103	0	
	- 181	895	3			+ 126	97987		
	- 30	194	2			- 75	- 236	1	
- 81	- 272	90922	2	Null 2-0		- 13	- 161	611	2
	- 143	93782	4			- 148	772	2	
	- 98	92035					99920		
	- 105	837	4			- 35	885	2	
	- 67	672	4			- 170	- 205	680	2
	- 133	94048	5			+ 08	- 197	483	1
	- 98	94181				- 277	- 340	100418	2
	- 146	93919	5			+ 88	- 63	758	3
	- 146	95248	2	Null 4-0			- 151	821	3
	- 106	95394						100972	
- 54	- 288	2				- 48	- 80	883	3
	- 180	128	4				- 137	746	3
	- 178	94050	0						
- 90	- 223	98058	0	Null 5-0					
	- 143	291	4					117754.43	<i>b</i>
	- 140	434	4					27419.50	<i>aa</i>
	- 151	98574						90334.93	0-0
	- 146	423	4					91653.27	1-0
	- 47	327	4					1318.34	2-0
	- 193	134	0					1281.47	02034.74
	- 104	05837	0					34.70	04181.45
	- 207							33.70	05304.46
	- 98	97104	3					33.06	06574.41
+ 13	- 130	421	2					32.48	07721.01
	- 152	570	2					32	08837.41
	- 107	615	1					32	1083.5
	- 118	497	2					32	100920.91
- 11	- 210	287	1					32	1051.5
	- 92								100972.41

Differences		Nulls	
		117754.43	<i>b</i>
		27419.50	<i>aa</i>
		90334.93	0-0
		91653.27	1-0
36.87	1318.34	02034.74	2-0
34.70	1281.47	04181.45	3-0
33.70	1246.71	05304.46	4-0
33.06	1213.01	06574.41	5-0
32.48	1179.95	07721.01	6-0
32	1147.50	08837.41	7-0
32	1115.5	1083.5	8-0
32	1051.5	100920.91	
32	100972.41		0-0

These differences are the same as in Table 6.

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Table 10. The Lyman Bands — Second Group

d_2	d_1	Lines	I		d_2	d_1	Lines	I	
	- 133	94048 94181	5	Null 3-0			75612 568		Null 3-5
		93919	5		- 57	- 101	487		
- 85	- 194	725	0		- 44	- 145	322		
- 89	- 270	446	0		- 54	- 199	128		
	- 388	078			- 52	- 251	74877 72620		Null 3-6
	- 137	89882	3	Null 3-1			- 52 568	1	
		90019			- 56	- 108	480	4	
- 55	- 91	89928	3		- 26	- 134	236	2	
- 45	- 146	782	3		- 48	- 182	144	3	
- 76	- 191	591	4		- 45	- 227	71017	1	
- 71	- 287	324	4						
	- 388	88986	1						
	- 120	85965 86094	2	Null 3-2					
	- 94	80000	2						
- 50	- 144	85856	3						
- 34	- 178	678	3						
- 71	- 249	420	3						
- 66	- 315	114	0	3-3 Band obscured by 1st Lyman Line					
	- 29	78825 78834	6	Null 3-4					
	- 46	808	2						
- 55	- 101	707	4						
- 58	- 159	548	3						

Differences		Nulls	
		94181.45	3-0
		90019.35	3-1
236.82	3925.28	86094.07	3-2
207.50	3717.78	82376.29	3-3
195.26	3522.52	78853.77	3-4
281.11	3241.41	75612.36	3-5
248.86	2922.75	72619.61	3-6

Table 11. The First Group of Lyman Bands

d_2	d_1	Lines	I*			Nulls	
- 39	+ 10	60780 60770	10d	Null 3-7	b-aa aa-aaaa	90334.93 20564.63	$B_0 - A_6$
	- 85	085	5			69770.30	$B_3 - A_7$
	- 124	501	4			67245.98	$B_3 - A_8$
	- 182	300	6			64857.66	$B_3 - A_9$
	+ 16	67202 67246	6d		2524.34 136.04 2388.30 132.20 2256.10	62601.56	$B_3 - A_{10}(a)$
	- 90	150	5				
	- 118	032	5				
	- 150	60873	10				
	- 193	080	5				
	- 232	448	5				
+ 105	+ 102	04050	3	Null 3-8	bbaa-aaaa	69770.30 6898.57	$B_3 - A_7$
	- 3	854	5			62871.73	$B_3 - A_{10}(b)$
		64858				1567.00	
	- 101	757	2			61304.73	$B_3 - A_{11}$
	- 122	035	3				
	- 148	480	4				
	- 180	303	2				
	+ 61	02752	4				
	+ 42	044	8				
		02002					
- 62	- 70	523	5	Null 3-10 (a)			
	- 141	382	3				
	+ 47	02020 02872	10d				
	- 36	836	6				
	- 84	752	4				
		01305					
	- 97	01208	6				
	- 100	108	5				
	+ 31	030	5				
Null 3-11							

* I indicates intensity.

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Table 12a. The *B-A* Emission Bands: Principal Series, from Lines as Classified by Jeppesen

R Branch				P Branch		
<i>d</i> ₂	<i>d</i> ₁	Lines		<i>d</i> ₂	<i>d</i> ₁	Lines
— 70.6 — 73.3		90208.2	0-0 Null			90208.2 90075.2
	— 202.4	90072.8 89872.4			— 133.0	
	— 273.0	89509.4			— 420.7	89258.3
	— 346.3	89253.1		— 64.4	— 485.1	88837.6 88352.5
				— 64.4	— 549.5	88803.5
		88048.2				88046.2
	+ 22.6	88068.8			— 123.0	85023.2
	— 29.3	86039.5		— 62.2	— 185.2	85738.0
	— 80.0	85930.2		— 71.3	— 256.5	85482.5
	— 72.4	85748.5		— 72.3	— 328.8	85153.7
— 51.9 — 80.0 — 68.8	— 181.7	85498.0		— 57.6	— 386.4	84767.3
	— 250.5					
		82132.7	2-0 Null			82132.7
	+ 19.1	82151.8			— 126.4	82006.3
	— 31.2	82120.6		— 47.5	— 173.9	81832.4
	— 63.2	82028.2		— 53.6	— 237.5	81594.9
	— 72.6	81800.2		— 66.1	— 303.8	81291.3
	— 66.3	81627.9		— 61.0	— 364.6	80926.7
	— 68.7	81336.9				
		78426.7				78426.7
— 51.9 — 62.3 — 53.0 — 45.7	+ 29.5	78456.2	3-0 Null			78316.9
	— 22.4	78433.8		— 52.5	— 162.3	78154.5
	— 85.9	78347.0		— 60.1	— 222.4	77932.1
	— 149.8	78198.3		— 56.6	— 270.0	77653.1
	— 195.5	77992.8		— 56.0	— 335.0	77318.1
		74957.6				
	+ 31.8	74980.4				74957.6
	— 19.0	74970.4		— 48.6	— 102.5	74855.1
	— 77.0	74893.4		— 54.0	— 151.1	74704.0
	— 129.0	74764.2		— 50.9	— 206.0	74498.0
— 50.8 — 58. — 52.2 — 56.8	— 186.0	74578.2		— 50.4	— 256.9	74241.1
		71711.8	4-0 Null			73933.8
	+ 36.6	71748.4				
	— 12.3	71736.1		— 47.1	— 92.4	71619.4
	— 64.7	71671.4		— 49.2	— 130.5	71470.9
	— 113.9	71557.5		— 48.5	— 188.7	71291.2
	— 152.7	71394.8		— 30.2	— 237.2	71054.0
	— 57.3	71184.8			— 277.4	70776.0

Table 12b. *B-A* Emission Bands (*Cont'd*): Principal Series, from Lines as Classified by Hyman

TABLES OF DATA

Table 12c. Nulls of the *B-A* Emission Series

Band No.	Nulls	Diff.	Diff.	Origin
	117754.43			<i>b</i>
	27419.50			<i>aa</i>
	90334.93			<i>b-aa</i>
	126.70			<i>bbaaa-baaaa</i>
0-0	90208.23			0-0 Null
1-0	86046.13	4162.1		<i>aaba-abba</i>
2-0	82132.68	3913.45	248.66	<i>baa-aaa</i>
3-0	78426.73	3705.95	207.50	<i>bab-aab</i>
4-0	74957.60	3469.13	236.82	<i>baaaa-aaaa</i>
5-0	71711.80	3245.80	223.35	<i>baab-aaab</i>
6-0	68702.82	3008.98	236.82	<i>baaaa-aaaa</i>
7-0	65917.17	2785.65	223.35	<i>baab-aaab</i>
8-0	63380.18	2536.99	248.66	<i>baa-aaa</i>
9-0	61080.01	2300.17	236.82	<i>baaaa-aaaa</i>
10-0	59061.04	2018.97	281.15	<i>bbb-abb</i>
11-0	57353.70	1707.34	311.63	<i>bba-aba</i>
12-0	55906.20	1447.50	259.84	<i>bbbb-abbb</i>

Table 13. Comparison of *B-A* Emission Bands Observed by Jeppesen with Lyman Bands Previously Reported by Others. Nulls by Venable

Band	Jeppesen			Dieke and Hopfield			Witmer		
3-0	Null	- 75.2	- 373.6	92098.5					
		- 88.8	- 208.4	93372.1					
		- 83.3	- 219.6	93671.5					
		- 130.3		93891.1					
				94027.4					
				94052.6	Null	- 133	94048.5		
							94181.52		
							93019		
							93725		
					- 85	- 194	93446		
3-1	Null			93075.0		- 279	93446		
			- 438.7	92030.3				- 368	
		- 74.0	- 512.3	92124.0				93078	
		- 66.5	- 578.8	91545.2				92037	
		- 74.0	- 274.8	80274.0					
		- 77.4	- 200.8	80540.7					
		- 77.7	- 123.4	80750.5					
		- 66.5	- 45.7	80873.9					
		+ 23.8	80919.6	80905.83	Null	- 137	80882	- 143	89876
							90010.4		90010
3-4	Null	- 122.6	80973.2	- 55	- 91	80928	Null	- 97	80922
		- 68.7	- 101.3	80951.9	- 45	- 146	80972	- 61	80704
		- 73.2	- 204.5	80317.4	- 70	- 191	80501	- 29	80577
		- 74.0	- 338.5	80807.8	- 71	- 267	80324	- 70	80314
		- 71.5	- 410.0	88508.0		- 338	88080	- 78	88078
		- 60.5	- 200.8	78383.1				- 68	88504
		- 59.0	- 140.5	78502.9					
		- 61.5	- 80.6	78712.4					
		- 54.7	- 28.1	78802.0					
		+ 25.6	78830.1	78804.51	Null	- 28	78825.8	- 22	78832
3-5	Null	- 102.0	78701.5	- 55	- 40	78808	Null	- 46	78854
		- 54.2	- 150.2	78545.3	- 55	- 101	78707	- 50	78808
		- 50.0	- 215.2	78330.7	- 58	- 150	78548	- 53	78703
		- 50.2	- 271.4	78058.3				- 57	78845
		- 57.3	- 328.7	77732.0				- 50	78830
		- 51.3	- 237.6	74033.1				- 50	78056
		- 52.0	- 186.3	75170.7				- 51	77781
		- 54.9	- 133.4	75357.0					
		- 50.0	- 78.5	75490.4					
		- 56.2	- 27.5	75608.0					
3-6	Null	+ 28.7	75501.4	75502.73	Null	- 44	75612	- 122	75400
							75508		
		- 95.8	75400.0	- 57	- 101	75467			
		- 40.0	75322.1	- 44	- 145	75622		- 147	75319
		- 52.7	75123.6	- 54	- 190	75123	- 51	- 198	75121
		- 58.1	74870.0	- 52	- 215	74877	- 54	- 252	74800

Table 14. *C-A* Absorption Bands

0-0 0-1 Nulls of Tables 14 and 15

		Lines		Lines			b aba	117754.43 18702.88
78	126	90165	2240	101405	Absorption	0-0	98.01.55	120.80
	48	90030						
Null		08001	2308	101200	Emission	0-0	90112.35	
	58	98033	2300	101242		4102.10	04950.25	
				101068		207.50	3054.00	01000.55
						250.84	3004.76	87305.70
						223.33	3471.43	83834.36
						230.34	3235.09	80500.27

Table 15. Principal Series of C-A Emission Bands

R Branch			Q Branch			P Branch		
		Lines			Lines			Lines
	Null	99112.35		Null	99112.35		Null	99112.35
	Null	94950.25		Null	94950.25		Null	94950.25
		95000.1			94771.8			94652.4
			- 48.2	- 151.3	94620.5		- 211.0	94441.4
			- 42.6	- 199.5	94421.0	- 40.0	- 257.0	94184.4
				- 242.1	94178.1	- 40.0	- 303.0	93881.4
	Null	91000.55		Null	91000.55		Null	91000.55
	+ 58.3	91058.8		- 49.2	90951.3			
- 48.5	+ 16.8	91076.6	- 41.3	- 90.5	90860.8			90730.8
- 47.1	- 30.3	91045.3	- 49.7	- 140.2	90720.6		- 102.7	90547.1
- 37.9	- 66.2	90977.1	- 32.3	- 172.5	90548.1	- 35.8	- 228.5	90318.3
			- 32.2	- 204.7	90333.4	- 33.7	- 202.2	90040.4
	Null	87305.79		Null	87305.79		Null	87305.79
	+ 60.8	87366.6		- 42.0	87263.8			
- 39.3	+ 21.5	87388.1	- 36.4	- 78.4	87185.4			87005.0
- 38.2	- 16.7	87372.4	- 42.0	- 120.4	87065.0		- 177.4	86887.0
- 41.1	- 57.8	87314.6	- 34.3	- 184.7	86910.3	- 34.0	- 211.4	86070.2
- 37.5	- 95.3	87219.3	- 36.4	- 191.1	86710.2	- 31.1	- 242.6	86433.8
	Null	83884.36		Null	83834.36		Null	83834.36
	+ 70.6	83905.0		- 32.5	83801.0			
- 47.6	+ 22.9	83927.9	- 35.5	- 68.0	83783.9			83613.0
- 39.4	- 16.5	83911.4	- 34.3	- 102.3	83631.6		- 100.1	83453.5
- 10.4	- 26.9	83884.5	- 35.3	- 137.6	83494.0	- 31.1	- 101.2	83202.3
	Null	80599.27		Null	80599.27		Null	80500.27
	+ 59.1	80658.4		- 32.9	80506.4			
- 23.8	+ 35.3	80693.7	- 22.8	- 55.7	80510.7			80380.8
- 35.3	0	80693.7	- 29.2	- 84.0	80425.8		- 142.3	80247.0
- 7.7	- 7.7	80680.0	- 25.6	- 110.5	80315.3	- 20.6	- 100.8	80078.7

Table 16. Hopfield's Band

Wave Length	I	Wave No.	Differences		Combination
		117754.43 417.04			b aabb
		117338.49			Null b-aabb
838.62	6	119243.51	1907.02		bb-aa
825.85	5	121087.36	1843.85	63.18	abaaa-baaaa
814.34	4	122801.84	1714.48	120.37	bbbbbb-babbb
803.86	3	124399.77	1597.93	116.43	abaaa-aaaaaa
794.23	2	125908.11	1508.34	89.59	babba-aabbb
785.75	1	127266.04	1358.83	149.51	babbb-aabba
778.18	0	128504.97	1238.03	120.80	abaab-aaaaab
771.35	0	129642.83	1137.86	100.17	abaaa-baaab

All of these allocations are subject to revision.

Table 17. The Principal Series of the Beta Band System
 Richardson page 172 Venable $bb-abba = 22271.31$

Branch Q							Branch R							Branch P						
	d_2	d_1	Lines	I	n		d_2	d_1	Lines	I	n		d_2	d_1	Lines	I	n			
0-0		Null	22271.31					Null	22271.31					Null		22130.30	3	2		
	- 8.00	203.25	9	1			+ 58.48	320.79	5	0			- 81.04	048.66	7	3				
- 7.98	- 10.04	247.21	5	2			- 8.87	49.61	379.40	8	1		- 88.48	21900.18	2	4				
- 7.87	- 23.01	223.30	4	3			- 0.32	40.20	419.00	2	2		- 7.03	865.07	2	5				
- 7.61	- 31.52	191.78	1	4			- 10.20	+ 30.00	449.78	3	3		- 90.11							
1-1		Null	21950.68					Null	21950.68					Null						
	- 7.88	061.80	10	1			+ 55.17	22014.85	2	0			V							
- 7.78	- 15.06	036.14	5	2			- 0.93	48.22	003.07	3	1		- 79.87	008.82	oa	3				
- 7.40	- 23.12	913.02	4	3			- 5.55	+ 42.67	105.74	1	2		- 85.20	583.02	oa	4				
- 7.56	- 30.07	882.35	1	4			- 8.96	+ 33.71	130.45	3	3		- 0.23		o	5				
2-2		Null	21658.17					Null	21658.17					Null						
	- 7.61	050.56	10	1			+ 49.58	707.75	2	0			V							
- 7.51	- 15.12	035.44	5	2			+ 43.81	751.56	0	1				21432.78	1	3				
- 7.47	- 22.50	012.85	3	3			- 5.77													
- 6.04	- 29.23	583.62	0	4																
3-3		Null	21360.05					Null	21360.05					Null						
	- 7.30	359.50	5	1			+ 43.00	410.61	3	0			V							
- 7.27	- 14.63	344.00	1	2			- 7.48	+ 30.18	440.70	8	1		- 00.40	21163.32	3					
- 7.22	- 21.85	323.11	2	3			- 7.53	+ 43.71	400.50	oa	2		- 00.40	006.02	4					
- 0.16	- 28.01	205.10	F	4																
4-4		Null	21085.04						20326.52					bb						
	- 7.13	078.81	0	1					7055.21					abba						
- 7.03	- 14.16	004.65	1	2																
- 6.90	- 21.12	043.53	1	3																
- 8.47	- 20.50	013.94	1	4																
5-5		Null	20815.45																	
	- 5.54	800.91	2	1				0.0	22271.31											
- 8.70	- 14.13	705.78	2	2				1.1	21950.68	311.63	bba-abaa									
- 5.78	- 19.01	775.87	0	3				2.2	21058.17	301.51	bbba-abaa									
- 11.32	- 31.23	744.64		4				3.3	21360.05	201.22	bbab-abab									
6-6		Null	20555.01						4.4	21085.04	281.01	bbb-abbb								
			553.00	1					5.5	20815.45	270.49	bbba-abba								
									6.6	20655.01	250.84	bbbb-abbb								

The series have been shortened to economize space. The horizontal differences of Table 5 apply. Richardson gives 114 lines in this sub-system. Lines marked V are by Venable. Nulls and null differences by Venable.

Table 18. The Principal Series of the Gamma Band System
 Richardson page 176 Venable $bb-aabba = 24847.54$

Branch Q					Branch R					Branch P				
	d_2	d_1	Lines	I	d_2	d_1	Lines	I	d_2	d_1	Lines	I	n	
0-0	Null	24847.54			Null	24847.54			Null	24707.83				
	- 8.16	839.38	4	1	+ 59.50	907.10	oof	0	- 8.10	- 82.80	924.04	2	2	
	- 8.15	16.31	823.07	3	2	- 10.78	48.80	955.90	4	- 9.05	- 91.05	533.80	4	4
	- 8.28	- 24.59	798.43	2	3	- 11.45	37.45	998.35	oof	- 9.54	- 100.50	433.30	5	5
	- 8.21	- 32.80	765.68	0	4	- 11.26	+ 25.19	25018.54	oof					
	- 7.98	- 40.78	724.90	oof	5									
1-1a	Null	24535.20			Null	24535.20			Null	24403.61				
	- 7.58	527.62	oa	v	+ 58.10	503.30	oof	0	- 7.09	- 70.75	320.80	3	2	
	- 8.12	- 15.70	511.92	1h	v	- 10.49	+ 47.61	640.91	oa	- 84.84	- 84.84	242.02	4	3
	- 13.85	- 29.05	482.87	o	v	- 9.73	+ 37.88	678.79	cof	- 3.04	- 81.80	100.22	5	5
2-2	Null	24207.20			+ .25	+ 37.53	712.32	o	2					
	- 8.37	198.83	of	1										
	- 7.58	- 15.95	182.88	3	2									
	- 8.47	- 24.42	158.36	0	3									
	- 8.63	- 33.05	125.31	0	4									
	- 8.21	- 41.26	084.05	of	5									
3-3	Null	23902.50												
	- 7.46	805.04	of	1										
	- 9.19	- 16.65	878.39	of	2									
	- 8.33	- 24.48	852.91	of	3									
	- 7.71	- 33.19	819.72	of	4									
1-1b	24521.55													
	- 7.58	513.07	1	1										
	- 7.44	- 15.02	498.95	oa	2									
	- 8.14	- 23.16	475.79	1	3									
	- 7.78	- 30.94	494.85	oo	4									
	- 7.13	- 38.07	406.78	1	5									
29326.52 4478.98					bb aabbba					29320.52 3093.05				
0-0					bb $bb-aabbba$					26232.57 224.34				
1-1a					$bbba-aabb$					- 8.23 16.46				
2-2					$bbaa-abab$					- 8.25 24.71				
3-3					$bbbaaaaab$					- 8.08 33.39				
0-0					24847.54					140.48 41.52				
1-1b					24521.55 323.99					107.96 22.38				

Table 20

 $bb-baa = 16891.42$

	Lines	I
Null	16891.42	
+ 59.56	950.98	0a
+ 55.45	17000.43	10
+ 54.42	060.85	5
+ 53.44	114.20	0
Null	16891.42	
+ 77.97	969.39	1
+ 56.02	17025.41	6
Null	17192.93	
+ 43.00	236.02	0
+ 42.99	279.01	7
+ 32.07	311.08	0
Null	17192.93	
+ 70.25	271.58	4
Null	17429.75	
+ 00.15	489.90	3
+ 82.41	575.31	10
Null	17420.75	
+ 68.63	497.72	5
Nulls		
20326.52		bb
12435.10		baa
16891.42		
17192.93	+ 301.51	
17429.75	+ 236.82	

Table 21

 $bb-aaa = 17140.08$

	Lines	I
Null	17140.08	
+ 59.20	190.28	10
+ 52.23	192.31	6
+ 78.42	218.50	8
- 48.79	081.20	8
- 55.42	084.56	2
Null	17388.74	
+ 62.75	451.52	10
+ 52.36	441.32	8
+ 70.80	450.70	2
bb	20326.52	
aaa	12186.44	
+ 248.00	17140.08	
	17388.74	

These all are direct departures
from the null.

Table 22

 $bb-baaa = 22234.83$

		Lines	I
	Null	22234.83	
- 0.51	- 9.40	225.34	10
	- 10.00	206.34	6
	- 22.61	183.74	00
	+ 40.61	284.02	8
	+ 58.80	343.81	0
	+ 06.50	410.40	10
	+ 71.31	481.70	0
	Null	22404.67	
- 0.64	- 5.03	489.64	7
	- 11.07	477.97	9
	- 11.24	455.06	0
	- 4.71	427.44	1
	+ 83.04	578.51	02
	+ 70.30	657.81	8
	+ 55.84	713.65	0
	+ 54.35	708.00	4
	bb	20326.52	
	baaa	7001.60	
	Null	22234.83	
	+ 259.84	22404.67	

Table 23

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Venable $ba-bbaa = 21621.84$

Branch R				Branch P					
Differences		Lines	I	n	Differences		Lines	I	n
	Null	21621.84				Null	21621.84		
	- 20.21	001.63	10	0		- 51.53	570.31	2	1
+ 4.05	- 16.15	585.48	8	1	+ 10.76	- 40.77	520.54	0	v
+ 4.13	- 12.02	573.46	10	2	+ 17.15	- 23.62	505.92	1	v
+ 9.39	- 2.63	570.83	5	3					
+ 15.42	+ 12.79	583.02	9	4					
+ 17.73	+ 30.52	614.14	5	5					
+ 10.70	+ 50.22	664.36	3	6					
+ 2.26	+ 32.78	642.92	5	6					
	Null	22555.95				Null	22555.95		
	- 36.87	519.10	2	0	+ 11.60	- 52.27	498.68	0h	v
+ 5.35	- 31.42	487.68	1	1		- 45.58	463.10	0h	v
+ 5.24	- 26.18	481.50	5	2					
+ 3.37	- 22.81	438.69	1	3					
+ 16.83	- 5.98	432.61	1	4					
+ 19.89	+ 10.91	443.52	0	5					
+ 15.72	+ 26.03	470.15	0	6					
+ 12.34	+ 38.97	510.12	1	7					
+ 46.52	+ 85.49	604.61	1	8					
	Null	23282.56				Null	23282.56		
	+ 17.85	300.41	0	0		- 40.56	242.00		
- 8.51	+ 0.34	309.75	0	1	- 7.05	- 47.21	194.20	00F	2
- 13.65	- 4.31	305.44	3	2	- 12.62	- 50.83	134.96		3
- 9.25	- 13.56	291.88	1	3	- 12.50	- 72.33	062.63		4
- 5.41	- 18.97	251.10	0	4	- 7.30	- 79.63	22983.00		5
- 2.76	- 21.75	244.75	0	5					
	Null	23803.62				Null	23803.63		
	- 6.20	797.34	3	0		- 45.47	758.16	0	v
- 1.13	- 7.42	789.92	1	1	- 16.44	- 81.01	606.25		2
- 14.09	- 21.51	768.41	2	2	- 12.13	- 74.04	622.21		3
- 10.86	- 32.37	736.04	12	3	- 11.78	- 86.82	535.39		4
+ 10.42	- 13.85	722.19	0	4					

<i>ba</i>	35375.28
<i>bbaa</i>	13753.44
	21621.84
<i>baaa-aab</i>	934.11
<i>baaa-bab</i>	720.61
<i>abb-aaa</i>	521.07
	23803.63

Richardson classified 237 lines belonging to 28 bands of this system separated by horizontal differences of Table 6. Bands of Tables 27 to 32 are departures from the null 21621.84.

Table 24

Richardson page 128

Venable *ba-aaa* = 23188.83

The null 24945.93 may require revision.

Table 25

Richardson page 128

Venable *ba-aaa* – 136.04

Branch R					Branch P				
d_2	d_1	Lines	I	n	d_2	d_1	Lines	I	n
		23188.83				Null	23052.70		
		138.04				- 36.86	015.03	1	1
	Null	23052.70				- 57.83	22058.10	3	2
- 21.47	+ 21.47	074.20	3	0		- 18.08	882.10	00a	3
	0	074.20	3	1		- 14.15	792.13	1	4
- 15.44	- 15.44	058.82	3	2		- 90.06			

Richardson classified 18 other lines related to these by differences in Table 6.

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Table 26

Richardson page 134

Venable *ba-aaa* - 438.54

Branch R					Branch P				
<i>d</i> ₂	<i>d</i> ₁	Lines	I	<i>n</i>	<i>d</i> ₂	<i>d</i> ₁	Lines	I	<i>n</i>
+ 15.44 + 13.42	Null	22750.29				Null	22750.29		
	+ 63.01	813.30	1	0	- 35.02	715.27	0	1	
	+ 78.55	891.85	1		- 18.12	697.15	2	2	
+ 25.26 + 17.59	+ 91.97	883.82	2		+ 20.39	+ 2.27	1	3	
	Null	23740.44	1	0	+ 16.90	699.42			
	+ 34.74	775.18	1		+ 15.35	717.04	4	4	
- 15.76 - 17.31 -.35 - 38.17	+ 60.90	835.18	1	1	+ 11.73	Null	23740.44		
	+ 77.59	912.77	1	2	+ 17.18	- 24.24	5	1	
	Null	24437.73	00	0	- 18.18	- 12.51	0	2	
- 15.76 - 17.31 -.35 - 38.17	+ 97.56	535.26	00	0	- 20.47	+ 5.67	0	3	
	+ 81.80	617.06	1	1	- 1.89	- 7.91	of	2	
	+ 64.49	681.55	2		- 18.18	- 8.62	0	3	
	+ 64.14	745.69	00	3	- 1.89	- 1.73	437.03	of	4
	+ 102.32	848.01	00	4					

<i>ba-aaa</i>	23188.83
<i>bbbb-aaab</i>	438.54
	<u>22750.29</u>
<i>abab-baa</i>	990.15
<i>aaaa-aab</i>	697.29
	<u>23740.44</u>
	<u>24437.73</u>

Richardson has classified 98 lines belonging to 22 bands in this system combined with the horizontal differences of Table 6. The bands here given are 0-0, 1-1 and 2-2.

Table 27

Richardson page 108
Venable *ba-bbaa* + 438.54

<i>d</i> ₂	<i>d</i> ₁	Lines	I	<i>n</i>	
+ 18.18 + 20.48 + 20.58	Null	22060.38			
	+ 63.89	124.27	1	v	0,0
	+ 82.07	206.34	6	2	
+ 102.55		308.89	2	3	
+ 123.13		432.02	3	4	
+ 15.02 + 14.73 + 21.68	Null	22980.79			
	+ 55.14	23015.93	1	v	1,1
	+ 70.16	086.09	1	2	
+ 85.89		172.98	00	3	
+ 107.57		280.55	1	4	
+ 125.56		406.11	0a	5	
+ 143.25		540.36		6	
<u>21621.84</u>					
<u>438.54</u>					
<u>22060.38</u>					
22960.79 900.41 = <i>baab-aab</i>					
Richardson gives 30 lines separated into 9 bands by the differences of Table 6.					

Table 28

Richardson page 102
Venable *ba-bbaa* + 185.44

<i>d</i> ₂	<i>d</i> ₁	Lines	I	<i>n</i>
	Null	21807.28		
	- 114.61	622.67	oa	v
+ 7.42	- 107.19	588.45	1o	1
+ 7.23	- 99.06	485.52	6	2
+ 6.55	- 92.41	393.11	3	3
+ 6.06	- 86.35	306.75	5	4
+ 11.90	- 74.45	222.31	2	5
+ 18.19	- 56.26	176.05	1a	6
	Null	22707.69		
	- 120.80	586.89	0	0
+ 19.75	- 101.03	485.86	1	
+ 13.64	- 87.08	398.28	2	
- 6.85	- 93.93	304.85	1	3
+ 2.41	- 91.02	213.83		4
<u>21621.84</u>				
<u>185.44</u>				
<u>21807.28</u>				
22707.69 900.41 = <i>baab-aab</i>				
Richardson classified this band as a <i>P</i> branch with the band of Table 23.				

Table 29

Richardson page 109

Venable $ba-bbaa + 281.11$

		Lines	I	n
$ba-bbaa$		21621.84		
$bbbabb$		281.11		
	Null	21902.90		
	+ 62.24	965.23	1	v
+ 3.82	+ 66.06	22301.20	4	v
+ 3.78	+ 70.84	102 13	2	P3
+ 15.28	+ 86.12	185.25	6	P4
+ 20.11	+ 106.33	294.48	1	P5
+ 20.92	+ 127.15	421.63	3	P6
		22204.48	1	R1
		22455.06	0	R2

Richardson gives 22 lines belonging to
8 bands separated by the difference num-
bers of Table 6.

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Table 30

Richardson page 104

Venable $ba-bbaa = 21621.84$

		Lines	I	n		$ba-bbaa$	21621.84
						$bcaa-acaa$	230.82
		Null	21858.66				21858.66
		- 28.10	830.56	5	1	bbaa-bbb	764.78
+ 25.53		- 2.57	827.99	10	2	abb-bab	648.28
+ 12.01		+ 9.44	837.43	6	3	abb-aaa	251.07
+ 15.89	+ 25.33	862.76	8	4			
+ 17.70	+ 43.02	905.79	3	5			
+ 18.31	+ 61.34	967.13	5	6			
+ 18.67	+ 80.01	22047.14	3	7			
+ 18.41	+ 98.42	145.56	3	8			
+ 18.76	+ 117.18	262.74	* 5	9			
+ 19.28	+ 126.46	399.20	1F	10			
+ 29.37	+ 155.83	555.03	1h	11			
+ 18.93	+ 174.86	729.89	1F	12			
		Null	22623.44				
		- 10.02	613.42	1	1		
+ 17.83		+ 7.81	620.69	4	2		
+ 8.88		+ 16.79	637.48	2	3		
+ 12.66		+ 29.45	666.93	2	4		
+ 14.56		+ 44.01	710.94	1F	5		
+ 15.31		+ 59.32	770.26	0	6		
		Null	23271.72				
		+ 3.86	275.58	ooF	1		
+ 9.41		+ 13.27	288.85	1	2		
+ 7.63		+ 21.90	310.75		3		
+ 10.50		+ 32.40	343.15	Oh	4		
+ 11.96		+ 44.36	387.51	oF	5		
+ 12.73		+ 57.09	444.60	00	6		
		Null	23792.79				
		+ 5.56	798.35	0	v		
+ 9.08		+ 14.64	812.99	3	2		
+ 9.17		+ 23.81	836.80	1	3		
+ 9.12		+ 32.93	869.73	1	4		
+ 10.07		+ 143.00	912.73	1	5		
+ 13.83		+ 53.83	966.56		6		
+ 17.61		+ 71.54	24038.10	oF	7		

The horizontal difference numbers of Table 6 combine with these band lines to give 25 other bands of which Richardson has classified 187 lines including those here given except one marked V.

Table 31

Richardson page 106
Venable $ba-bbaa = 149.93$

		Lines	I	n
		Null	21771.77	
		+ 17.84	789.61	1
		+ 26.00	815.61	2
		+ 6.02	32.02	3
		+ 5.03	37.06	4
		+ 8.67	45.72	5
		Null	22516.19	
		+ 43.83	560.02	1
		+ 31.76	508.72	2
		+ 20.37	612.15	3
		- 15.97	616.55	4
		- 7.63	613.42	5
		Null	23280.07	
		+ 26.86	307.83	0
		+ 17.21	325.04	v
		- 6.55	325.70	2
		- 10.66	343.30	3
		+ 3.06	352.77	4
		+ 1.87	359.33	5
		- 2.91	359.33	6
			21621.84	
			149.93	
		abaa-abb	21771.77	0, 0
		bbaa-bbb	22516.19	1, 1
			23280.07	2, 2

Richardson page 126

Venable $ba-bbaa + 195.26$

Branch R					Branch P				
		Lines	I	n			Lines	I	n
- 16.58	Null + 20.21 + 4.63	21420.58 446.79 451.42	8 5 1	0 1	- 15.81 - 15.75 - 13.84	Null - 40.04 - 55.85 - 71.62 - 85.46	21420.58 380.54 330.09 259.07 173.61	4 6 5 3	1 2 3 4
- 16.64	- 11.11	440.31	8	2					
- 18.83	Null + 22.83 + 4.00	22334.70 357.53 361.53	2 1 1	0 1 1	- 23.54 - 62.97	Null - 31.97 - 55.51 - 118.48	22334.70 302.73 247.21 128.73	00 5 5	1 2 3
- 10.22	- 6.22	355.21	3	2					1
- 12.76	Null - 6.75	23235.11 228.86	3	0					
- 12.76	- 19.51	208.85	0	1					
- 0.44	- 28.05	179.00	2	2					
- 12.82	- 41.77	138.13	00	3					
- 15.48	- 57.25	080.88	0	4					
					ba-bbaa bab-aaba bbbb-bab baab-aab		21021.84 195.26 Null 908.12 900.41	21420.58 22334.70 22235.11	0-0 1-1 2-2

Table 33

Richardson page 128
2,0 Band, Table XXVIVenable $ba-bbaa + 5095.81$

Branch R				Branch P				
	Lines	I	n			Lines	I	n
+ 11.80	26716.59 728.48	0	0			20710.59 673.14	ooF	1
				- 17.34	- 43.45	612.35	1	2
				- 22.76	- 60.70	520.80	00	3
				- 17.33	- 82.55	429.02	0	4
					- 99.88			
						ba-bbaa aaa-baaa	21021.84 5094.75	
							20710.59	

The horizontal difference system of Table 6 combines with the principal series of Tables 32 and 33.

Table 34

Venerable *ba-aba*

Table 35

Richardson page 189
1-0 branches only

Venerable *ba-abb* = 22687 78

Branch R					Branch P				
		Lines	I	n			Lines	I	n
	Null	22667.76				Null	22667.76		
- 15.73	+ 54.89	722.65	1	0		- 64.94	602.82	2	1
	+ 39.16	761.81	2	1	- 14.72	- 79.66	523.16	2	2
					- 12.40	- 92.06	431.10	4	3

35375.27 ba
12707.51 abb
22667.76

The horizontal differences of Table 5 (not Table 6) combine with these branches

Table 36

Dieke $3d'\Sigma \rightarrow 2p'\pi$ Venable $bba-bab = 12709.43$

n	Branch R				Branch Q				Branch P			
	d_2	d_1	Lines	I	d_2	d_1	Lines	I	d_2	d_1	Lines	I
1	Null	12700.43			Null	12709.43			Null	12709.43		
2	- 33.76	675.67	3		- 55.17	654.26	7		- 48.87	660.56	0	
2	- 24.07	68.43	616.24	8	- 43.74	98.91	555.35	2	- 82.94	131.30	529.26	00
3	- 13.31	71.74	545.50	4	- 16.81	115.72	430.63	5				
4	- 6.43	78.17	407.33	7	- 11.13	126.85	312.78	2				
5	- 2.94	81.10	386.23	4	- 4.24	131.00	181.00	3				
1		12588.75	1			12574.51	4			12586.99		3
2	- 70.12	518.63	5		- 99.74	474.77	1		- 121.13	455.86		
2	- 17.47	87.50	431.04	5	- 24.71	124.55	350.22	4b	- 26.57	158.30	297.16	
3	- 1.53	89.12	341.92	7	- 15.40	140.07	210.18	0	- 21.43	180.13	117.03	
4	- 0.90	00.02	252.90	2	- 1.80	141.84	068.34	1				
1		12519.08	0			12475.72	5					
2	- 43.06	475.72	5		- 64.40	411.32	00			12365.12		2
2	- 22.45	06.41	409.31	1	- 32.20	96.00	314.72	0		252.81	od	
3	- 50.12	126.53	282.78	4					66.92	- 112.81	072.58	1

<i>bba</i>	10074.5
<i>bab</i>	0305.08
<i>0-0 Null</i>	12709.43

The three bands given above are those classified by Dieke as 0-0, 1-1 and 2-2. The difference system of Table 7 combines with each of these to give other bands in horizontal sequence.

Further departures from the 0-0 null 12709.43 give the sub-system of Tables 37, 38, 39, and 40.

The second differences in this system are so irregular that I have not been able to evaluate the nulls of the subordinate bands. The comparative regularity of the horizontal differences, however, leaves little doubt that Professor Dieke's classification is correct.

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Table 37

Dieke $3d'\pi^- \rightarrow 2p'\pi^+$

Branch R					Branch Q					Branch P				
n	d_2	d_1	Lines	I	d_2	d_1	Lines	I	d_2	d_1	Lines	I		
		Null	12709.43			Null	12709.43							
			281.11				248.66							
		Null	12990.54			Null	14958.00							
1	+ 6.24	998.78	10		- 37.27	920.82	5							
2	- 3.30	+ 2.94	999.72	9	- 11.76	49.03	1					800.50	2	
3	- 6.90	- 4.06	995.06	10	- 10.39	59.42	4					694.18	6	
4	- 5.20	- 9.26	980.40	9	- 5.50	65.92	1					570.37	2	
5	- 4.32	- 13.58	972.82	10	- 2.02	68.54	1					400.70	4	
6	- 3.92	- 17.40	955.42	5	- 4.77	- 73.31	2					340.04	0	
7	- 3.53	- 20.93	934.49	9								+ .45	- 119.40	1
8	- 3.39	- 24.32	910.17	0								221.54		
9	- 3.15	- 27.47	882.70	2										
10	- 3.07	- 30.54	852.10	00										
		Null	12783.04			Null	12735.76							
1	+ 12.45	796.52	7		- 21.23	714.53	2							
2	- 1.42	+ 11.02	807.54	3	- 15.89	- 36.62	1					600.52	1	
3	- 8.87	+ 2.15	809.69	7								500.64	5	
4	- 6.80	- 4.65	805.04	3								- 0.74	- 100.02	1
5	- 5.51	- 10.16	794.88	5								- 5.73	- 106.35	2
6	- 4.66	- 14.82	780.06	2								- 2.05	- 109.30	0
7	- 4.14	- 18.06	761.10	2								- 1.06	- 110.30	00
8	- 3.64	- 22.80	738.50	1								083.01		
9	- 3.47	- 26.07	712.43	1										
		Null	12546.22			Null	12498.94							
1	+ 23.42	569.64	5		- 13.20	485.08	2							
2	- 6.07	+ 17.35	586.99	3	- 13.30	- 26.05	0					377.33	2	
3	- 9.22	+ 8.13	595.12	5								298.04	4	
4	- 7.71	+ .42	595.54	1								- 18.88	- 98.17	1
5	- 6.49	- 0.07	589.47	3								- 13.69	- 84.48	2
			577.92	0								- 14.08	- 98.50	ood
			561.61	1								- 1.02	- 09.68	11910.15
			541.25	00										1
			517.54	00										
		Null	12410.43											
1		- 47.19	363.24											
2	+ 14.25	- 33.94	329.30	3										
3	+ 11.02	- 22.92	306.48	2										
4	+ 12.44	- 10.48	296.00	2										
	Nulls		12990.54	0-0			12958.09	0-0						
			12783.04	1-1			- 223.33	12735.76	1-1					
			12546.22	2-2			- 236.82	12498.94	2-2					
			12410.43	3-3										

The nulls of the P branches are doubtful as there are no P_1 lines.

The lines of the 3-3 R branch are reversed from the order given by Dieke. See text.

Table 38

Dieke $3d'\pi^+ \rightarrow 2p'\pi^-$

Branch R					Branch Q					Branch P				
d_2	d_1	Lines	I		d_2	d_1	Lines	I		d_2	d_1	Lines	I	
		12709.43 +311.63					12709.43 +236.82							
	Null	13021.06			Null		12940.25							
- 44.32	+ 109.23	130.29	10	- 12.58	+ 38.11	984.36	6							
- 16.36	+ 4.91	195.20	10	+ 25.53	13009.89	0								
- 11.47	+ 48.65	243.75	8	- 17.79	+ 7.74	017.63	10							
+ 6.54	+ 20.02	263.77		- 14.35	- 6.61	011.02	8							
	+ 20.56	290.33	10	- 35.33	- 32.04	12978.08	10b							
				+ 7.32	- 24.02	953.46								
				+ 13.55	- 11.07	942.30								
		12896.18	2			12767.61	1							
- 30.41	+ 31.36	927.54	7	- 37.36	+ 14.49	782.10	00							
	+ .05	928.49	9	- 22.87	759.23	0								
		12720.54	0			12505.54	1							
	+ 38.01	756.55	1			504.30	0							
		741.78	1											

Table 39

Dieke $3d'\Delta^- \rightarrow 2p'\pi^-$

Branch R					Branch Q					Branch P				
n	d_2	d_1	Lines	I	d_2	d_1	Lines	I	d_2	d_1	Lines	I		
1			13375.10	0										
2	+ 96.11	471.21	2				13250.12	10						
3	- 2.38	+ 99.73	564.04	10		+ 33.48	283.60	10						
4	- 4.82	+ 88.01	053.85	4	- 1.30	+ 32.09	315.60	10						
5	- 0.33	+ 82.58	730.45	6	- 2.44	+ 20.65	345.34	2		+ .90	- 20.70	030.09	10	
6			811.73	1	- 0.20	+ 23.45	368.70	2		- .90	- 21.00	008.43	1	
7			878.05	2	- 0.77	+ 16.08	385.47	2		+ 1.03	- 23.20	985.14	8	
1			13261.88	10										
2	+ 81.04	342.02	4				13143.25	10						
3	- .07	+ 80.37	423.20	4		+ 22.10	165.35	0						
4	- 3.45	+ 76.02	500.21	1	+ 2.51	+ 24.61	189.06	10						
5					- 3.10	+ 21.51	211.47			+ 2.29	- 28.19	016.31	7	
6										+ .46	- 27.73	888.51	0	
1			13150.41	10										
2	+ 66.70	226.20	0				13048.76	10						
3	- .86	+ 65.03	202.13	10		+ 18.21	066.97	10						
4					- 35.21	- 17.00	049.07	10						
5										+ 2.00	- 38.76	849.04	1	
										+ 3.00	- 36.67	812.37	2	

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Table 40

Dieke $3d'\Delta^+ \rightarrow 2p'\pi$

Branch R					Branch Q				Branch P			
n	d_4	d_1	Lines	I	d_4	d_1	Lines	I	d_4	d_1	Lines	I
1			13384.68	5			13284.38	9				
2	- .45	+ 114.09	498.77	4		+ 56.73	321.11	10			13076.83	10v
3		+ 113.44	612.21	5		+ 7.63	+ 64.36	2		- 4.90	071.93	10
4						- 22.87	+ 41.60	2		+ 4.90	076.83	10v
5							427.18		- 17.09	- 12.19	064.64	10
1			18263.77	10			13149.84	8				
2		+ 84.70	348.47	6		+ 30.38	180.22	10			13972.25	4
3	- .81	+ 83.89	432.36	3		+ .87	+ 31.25	9		- 25.38	946.87	9

Table 41

Dieke $2S'\Sigma \rightarrow 2p'\Sigma$ Venable $bbaa-aabb = 13335.50$
2-0, 3-1, and 4-2 bands

Branch R					Branch P				
d_4	d_1	Lines	I	n	d_4	d_1	Lines	I	n
- 21.72	Null	13335.50				Null	13335.50		
	+ 86.59	402.09	10	0	- 18.28	317.22	10		1
	+ 44.87	447.76	10	1	- 31.31	285.01	10b		2
- 22.10	+ 22.57	470.33	10	2	+ .83	30.48	255.43	10	3
					- 21.88	- 51.86	203.50	10	4
- 15.08	Null	13856.57			Null	13856.57			
	+ 36.87	893.44	10	0	- 30.27	826.20	10		1
	+ 21.79	915.23	9	1	- 43.20	783.00	10		2
- 11.36	+ 9.43	924.66	10	2	- 7.45	- 50.68	732.32	10	3
					- 10.89	- 61.57	670.75	10	4
- 12.29	Null	14621.45			Null	14621.45			
	+ 24.93	646.38	5	0	- 34.13	587.32	4		1
	+ 12.64	658.02	4	1	- 46.44	540.88	5r		2
- 14.07	- 1.43	656.59	6	2	- 10.28	- 57.72	483.16	5	3
	- 15.68	640.91	4	3	- 11.69	- 60.41	413.75	9	4
					- 11.36	- 81.77	331.08	4	5
					$bbaa$	13753.44			
					$aabb$	417.94			
					$abb-aaa$	13335.50	0-0		
					$bbaa-bbb$	13856.57	1-1		
						764.78	2-2		

Dieke combines this system with that of Table 42. The horizontal difference system of Table 6 applies. Note that the second differences in this table are negative; those of Table 42 positive. Also note the intensities.

Table 42. Extrapolated from Dieke $2S'\Sigma \rightarrow 2p'\Sigma$. 0-0 and 1-0 bands
 Venable $bbaa-bbbb = 6480.24$

Branch R					Branch P				
d_2	d_1	Lines	I	n	d_2	d_1	Lines	I	n
	Null	7648.36				Null	7648.36		
+ 31.43	+ 57.98	706.34	5	0	+ 32.58	- 42.49	805.87	3	1
+ 25.35	+ 89.41	795.75	4	1	+ 26.83	- 9.91	595.96	5	2
+ 24.36	+ 114.76	910.51	7	2	+ 26.80	+ 16.92	612.88	3	3
+ 22.39	+ 130.12	8040.03	3	3	+ 26.41	+ 43.81	726.91	5	5
+ 21.67	+ 102.51	212.14	6	4	+ 26.41	+ 70.22	726.91	5	5
	+ 183.56	396.72	1	5	+ 26.15	+ 96.37	823.28	4	6
	Null	8802.29				Null	8802.29		
+ 27.98	+ 54.41	750.70	96	0	+ 19.33	- 38.20	564.09	4	1
+ 25.16	+ 82.87	833.07	8	1	+ 21.89	- 8.87	645.22	9	2
+ 19.44	+ 107.53	940.00	10b	2	+ 26.58	+ 13.02	658.24	7	3
+ 21.04	+ 126.97	9007.57	6	3	+ 21.20	+ 39.80	697.84	10b	4
+ 6.95	+ 148.01	215.58	8	4	+ 60.80	758.64		5	5
	+ 154.99	370.67	5	5					

For Dieke's 2-0 band see Table 41.

$bbaa$	13753.44
$bbbb$	7273.20
$bbba-aab$	1168.12
$bbaa-abb$	1043.93

6480.24	0-0
7648.36	1-1
8802.29	2-2

The intensities are those of the 0-0 and 1-0 bands of Dieke. The wave numbers are extrapolated, given by using the difference system of Table 6, which applies to this system. The P series is longer than given above. The principal series given above is too far in the infrared for observation. Dieke measured and classified 118 lines. See *Phys. Rev.*, Nov. 1, 1936, page 708. See also Table 41.

Table 43. Extrapolated from Richardson's Table LXI by Use of the Horizontal System of Table 5

R Branch			n	P Branch			n
		9082.67		1-1		9082.67	
	51.59	134.36	0		64.74	017.93	1
9.93	42.38	176.74	1	8.42	73.16	8944.77	2
10.05	31.43	208.17	2	9.37	82.53	882.24	3
12.06	19.37	228.54	3	8.53	91.06	771.18	4
11.09	8.28	237.82	4	7.40	98.46	672.72	5
9.92	- 1.65	236.17	5				
		8756.06		2-2		8756.06	
	49.61	805.67	0		60.49	695.57	1
10.11	34.50	845.17	1	9.56	70.05	625.52	2
10.80	28.70	873.87	2	8.85	78.93	540.50	3
10.81	17.89	891.36	3	8.58	87.51	459.08	4
11.11	6.78	898.64	4	7.99	95.90	363.58	5
		8427.9		3-3		8427.9	
	45.9	473.8	0		58.2	360.7	1
9.8	36.3	510.1	1	8.6	66.8	302.9	2
10.7	25.6	535.7	2	9.4	76.2	226.7	3
10.6	15.0	550.7	3	8.6	84.8	141.9	4
11.3	3.7	564.4	4	7.3	92.1	049.8	5
9.9	- 6.2	548.2	5				
		8089.5		4-4		8089.5	
	43.7	133.2	0		54.6	034.0	1
10.4	33.3	166.5	1	8.9	63.5	7971.4	2
10.3	23.1	189.5	2	10.0	73.5	807.9	3
11.3	11.7	201.2	3	7.7	81.2	816.7	4
		7736.0		5-5		7736.0	
	39.3	775.3	0		53.4	682.6	1
6.9	32.4	807.7	1	6.8	60.2	622.4	2
6.8	25.6	833.3	2	8.1	68.3	554.1	3
		13753.44			bbaa		
		4360.27			aaaaab		
Null	0-0	9384.17					
"	1-1	9082.67		301.50	bbbaa-abaa		
"	2-2	8756.06		326.61	bbbaa-abbb		
"	3-3	8427.97		328.09	bbbaa-abab		
"	4-4	8089.5		338.47			
"	5-5	7236.0		353.5			

Table 44

Richardson, page 122					Venable (<i>ba-bbaa</i>) — (<i>abb-abbb</i>)				
<i>d</i> ₂	<i>d</i> ₁		I	<i>n</i>	<i>d</i> ₂	<i>d</i> ₁		I	<i>n</i>
		27310.09						27310.09	
+ 50.19	- 108.49	207.60	7	0					
+ 43.40	- 58.30	140.30	1	1	+ 38.90	- 131.72	184.37		1
+ 13.88	- 14.80	134.40	5	2	- 42.08	- 92.82	001.55		2
+ 10.36	- 1.02	133.38	1	3	+ 45.10	- 134.50	20957.05		3
+ 10.79	+ 18.34	151.72	1	4	+ 26.58	- 89.40	867.65		4
+ 19.67	+ 38.13	180.85	0a	5	+ 11.97	- 62.82	794.88		5
	+ 57.80	247.65	0a	6		- 50.85	743.98	00	6
<i>ba-bbaa</i>		21621.84						27575.93	
<i>abb-abbb</i>		5094.25							
<i>bbbb-abbb</i>		27310.00			+ 40.55	- 131.90	444.03	rd	1
		250.84			+ 34.82	- 191.35	352.08	OF	2
		27575.93			+ 52.25	- 56.53	296.15	0a	3
					+ 42.24	- 4.28	291.67	1a	4
						+ 38.16	330.03	2F	5

Table 45

Branch <i>R</i> , Richardson, page 136					Branch <i>Q</i> , Richardson, page 122				
<i>d</i> ₂	<i>d</i> ₁		I	<i>n</i>	<i>d</i> ₂	<i>d</i> ₁		I	<i>n</i>
		27474.48						27474.48	
+ 10.51	+ 12.77	487.25	1	0					
+ 27.22	+ 23.28	510.53	OF	1	+ 64.33	- 120.48	347.00	0	1
	+ 50.50	561.03	OF	2	+ 54.00	- 03.15	283.85	3	2
					+ 24.52	- 8.25	275.00	1	3
						+ 16.27	291.87	1a	4
+ 11.00	+ 19.17	27162.91	0h	0	<i>ba-bbaa</i>				
+ 5.44	+ 31.10	181.08	1h	1	<i>abb-aaaa</i>				
	+ 36.00	212.24	0a	2	<i>bba-aba</i>				
		248.84			21621.84				
					5852.84				
					27474.48				
					311.57				
					27162.91				

The horizontal system of Table 6 combines with the vertical series of both Tables 44 and 45. Where no intensities are given the lines are obtained by extrapolation.

Table 46

0-0 Band of Richardson's Table XXVIII				
R Branch			P Branch	
		29320.52		
		4430.78		
		24805.74		24805.74
		933.37		857.55
- 6.00	+ 37.03	905.00	2	2
	+ 31.03	25015.71	1a	1a
		25015.71	OF	OF
		— 3.17		— 38.10
		— 4.14		— 40.36
		— 4.47		— 44.50
		+ 2.23		— 48.07
		— 20.03		— 46.74
				— 24.71
				652.27
Q Branch			The R and P branches are confirmed by the horizontal differences of Table 6. The Q branches, suggested by Venable, are not so confirmed.	
		24805.74		
		889.82	2	
		875.42	2	
		847.97	0	
		813.22	00	

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Table 47

0-0 Band of Progression Classified by Richardson on page 132 of His Book				
	29326.52 4580.04			In the absence of lines near to the null it is impossible to fix the null by extrapolation. The level $bbaaa$ 4380.04 is doubtful.
+ 43.88	- 81.62	24746.48	Null Q 1 Q 2 Q 3 Q 4 Q 5 Q 6	
+ 36.52	- 37.74	24131.48		
	- 1.22	049.86		
		012.12		
		010.90		

Table 48. Comparison of Bands of Hydrogen and Deuterium

Alpha Bands R 0-0 Branch						
Hydrogen			Deuterium			
Differences	Lines	I	Diff.	I	Lines	Differences
Null	16619.01		+ 46.89		10665.90	Null
+ 59.56	16678.57	10	+ 17.10	4	16695.80	+ 20.96
+ 51.08	16730.55	10	- 18.58	2	16721.07	+ 26.11
+ 43.87	16774.42	6	- 30.28	3	16744.14	+ 22.17
+ 33.28	16809.70	6	- 47.38	2	16762.32	+ 18.18
+ 26.34	16836.04					- 3.85
+ 18.07	16853.01	1				- 3.94
+ 7.13	16860.14	1				- 3.99
- 3.20	16850.01	1				

Principal Nulls in Vertical Sequence

Diff.	Nulls	Diff.	Nulls	Diff.
- 281.11	16619.01	+ 46.89	1065.90	
- 270.54	16332.90	+ 131.00	1644.59	- 201.31
- 259.79	16007.38	+ 201.33	16268.69	- 19.90
- 248.66	15807.57	+ 270.35	16077.97	- 190.72
- 236.82	15558.91	+ 333.79	15802.70	- 185.27
- 223.33	15327.09	+ 390.70	15712.79	- 170.91
	14098.76	+ 440.08	15538.84	- 173.95

Horizontal Combining System

Diff.	Nulls	Diff.	Nulls	Diff.
- 136.04	2425.34	- 709.44	1814.00	
- 132.20	2388.20	- 642.61	1745.69	- 69.11
- 129.34	2256.10	- 577.86	1678.20	- 67.53
- 127.31	2126.76	- 514.67	1612.09	- 66.17
- 126.70	1989.43	- 453.46	1545.97	- 66.12
- 127.77	1872.75			
	1744.98			

Table 49. Comparison of Levels of Hydrogen and Deuterium

	Hydrogen		Diff.	Deuterium	
	Differences	Levels		Levels	Differences
b		117754.43	+ 303.57	118118.	
a		109078.	+ 30.05	109708.05	
ba	90334.93	35375.37	- 618.00	34756.41	
bb	98991.55	20326.52			
aa		27419.50	+ 7.01	27427.01	
ab					
bba	21621.84	19074.51			
aba	16619.01	18762.88	+ 18.12	18781.	
bbb		12088.00			
abb		12707.51			
baa		12435.10	- 60.00	12375.04	
aaa		248.66	+ 3.33	12189.77	185.27
bab		0305.08			
aab		0157.58			
bbaa		13753.44	- 435.03	13317.41	
bbab		13710.57			
abaa		301.51			
abab		13451.03			
bbbb		13425.35			
bbba		7325.70			
bbbb		7273.20			
abba		270.40			
abbb		7055.21			195.00
baaa		250.84			190.72
baab		7013.30			
aaaa		7001.00	- 55.03	7030.00	
aaab		7057.00			
aaab		230.82	+ 1.88	0850.75	179.01
aaab		0834.00			173.46

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Table 50. Calculated Levels of Mixtures of Hydrogen and Deuterium Corresponding to the Lyman, Balmer, Paschen and Brackert Levels of Hydrogen, Assuming $H\alpha = 15233.094$ and $D\alpha = 15237.230$

<i>c</i>	109708.056			<i>a</i>	109678.276		
<i>ca</i>	27449.250	<i>cc</i>	27427.014	<i>aa</i>	27419.569	<i>ac</i>	27397.333
<i>cca</i>	12212.120	<i>ccc</i>	12189.784	<i>aaa</i>	12187.520	<i>cac</i>	12185.190
<i>aca</i>	12210.900	<i>acc</i>	12188.580	<i>aaa</i>	12188.475	<i>aac</i>	12184.139
<i>ccaa</i>	6880.537	<i>ccoa</i>	6856.945	<i>aaaa</i>	6855.937	<i>caca</i>	6832.351
<i>ccac</i>	6880.469	<i>cccc</i>	6855.783	<i>caac</i>	6855.860	<i>cacc</i>	6832.159
<i>acaa</i>	6879.317	<i>acca</i>	6855.741	<i>aaaa</i>	6854.892	<i>aaca</i>	6831.300
<i>acac</i>	6879.249	<i>accc</i>	6855.549	<i>aaac</i>	6854.824	<i>aacc</i>	6831.108

Possible Lines Corresponding to $H\alpha$ and $D\alpha$ in Mixtures

Combination	Calculated	Observed	Ascribed to
<i>ca-aac</i>	15285.211	15285.08	
<i>ca-cac</i>	284.180	284.39	D
<i>ca-aaa</i>	262.875	262.28	
<i>cc-acc</i>	262.875	263.36	
<i>ca-aaa</i>	261.830 }	261.52	
<i>cc-cac</i>	261.830 }	260.76	HD
<i>ca-acc</i>	260.770	260.76	HD
<i>ca-ccc</i>	259.470	259.06	D
<i>aa-aac</i>	255.430	255.48	HD
<i>aa-cac</i>	254.38	254.18	HD
<i>cc-aaa</i>	240.539	240.54	HD
<i>cc-aaa</i>	239.49	-----	
<i>ca-aaa</i>	238.43	-----	
<i>cc-acc</i>	238.43	-----	
<i>ca-cca</i>	237.230 }	237.23	
<i>cc-ccc</i>	237.230 }	237.23	D α
<i>aa-aaa</i>	233.094 }	233.094	
<i>ac-aac</i>	233.094 }	233.094	H α
<i>ac-cac</i>	232.04	-----	
<i>aa-eaa</i>	232.04	-----	
<i>aa-acc</i>	230.99	-----	
<i>aa-ccc</i>	229.785	-----	
<i>cc-aca</i>	216.11	216.38	D
<i>cc-eca</i>	214.994	214.73	D
<i>ac-aaa</i>	210.758	210.51	D
<i>aa-eaa</i>	209.71	209.58	HD
<i>ac-acc</i>	208.65 }		
<i>aa-aca</i>	208.65 }		
<i>ac-ccc</i>	207.449	207.85	D
<i>aa-cca</i>	207.449	207.13	HD
<i>aa-aea</i>	186.33	186.47	HD
<i>ac-cca</i>	185.213	184.90	D

Table 51. Calculated Lines Corresponding to the Second Balmer Line for Mixtures of H and D

aa-aaaa	20618.142	ac-aacc	20566.225
aaaa	617.950	aaaa	566.038
cacc	617.091	cacc	505.174
caca	616.809	caca	504.892
cc-aacc	595.906	aa-acac	564.745
aaaa	595.714	aaaa	504.677
cacc	594.855	cccc	564.020
caca	594.603	ccca	563.828
ca-aaaa	594.426	aaaa	503.700
aaaa	594.358	aaaa	503.032
cccc	503.701	cccc	502.816
ccca	503.500	ccca	502.024
caac	503.381	cc-acac	547.765
caaa	503.313	aaaa	547.697
cccc	502.497	ccac	546.645
ccca	502.705	ccaa	546.477
aa-accc	588.461	ac-aaaa	542.509
aaaa	588.200	aaaa	542.441
cacc	587.410	cccc	541.784
caca	587.218	ccca	541.502
cc-aaaa	572.190	caac	541.469
aaaa	572.122	aaaa	541.396
cccc	571.465	cccc	540.580
ccca	571.273	ccca	540.385
caac	571.145	aa-acac	540.320
caaa	571.077	aaaa	540.252
cccc	570.261	ccac	539.100
ccca	570.009	ccaa	539.032
ca-acac	570.001	ac-acaa	518.084
aaaa	509.933	ac-acaa	518.016
ccac	568.781	ccac	516.864
ccaa	568.713	ccaa	516.796

Table 52. Levels of Line Molecules of Sub-atom 2 and Hydrogen
All in the α Configuration

H	Diff.	He +	Diff.	$a8a_2$	Diff.	$a4a_2$	Diff.	$a2a_2$
100678.00	45.22	438802.88 100723.22 48705.87						
27419.50	11.30	27430.80 17555.71					20.10	27456.97 He 3D
12180.44	5.23	12101.47 8057.		He 3F 6858.22	14.28	He 1D 12205.78	3.31	12200.09
0854.87	2.13	6857. 5418.43	1.22	He 1F 4388.03	6.07	0804.20	1.88	6800.17
4387.12	1.81	3027.21		4300.69	1.77	4302.40	1.06	4302.52
3040.01	1.26	3047.87 2597.				3040.98	.65	3050.03
2238.33	.02	2230.25				2240.60	.31	2241.00

Compare He 1F 6857.76 with $8a_2$ 6857.
He 3F 4380. with $10a_2$ 4388.03

The discrepancies are within the probable errors of Fowler's levels.

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Table 53. Levels of the Helium Line Spectrum

Doublet System			m	Singlet System	
Quantum No.		Wave No.		Wave No.	Quantum No.
1.6888		38		1S	
1 + 1.6974	2.6974	38454.08	2	32033.30	1.8503
2 + 1.6999	3.6999	15073.92	3	13445.94	1 + 1.8560
3 + 1.7007	4.7007	8012.54	4	7370.50	2 + 1.8575
		4963.67	5	4047.22	3 + 1.8588
		3P		1P	
1.9372		29223.87	2	27175.85	2.0080
1 + 1.9339	2.9339	12746.08	3	12101.38	1 + 2.0105
2 + 1.9321	3.9321	7093.58	4	6818.05	2 + 2.0108
3 + 1.9314	4.9314	4509.93	5	4308.25	3 + 2.0108
		8D		1D	
2.9972		12209.09	3	12205.78	2.9978
1 + 2.9967	3.9967	6866.17	4	6864.29	1 + 2.9980
2 + 2.9964	4.9964	4393.52	5	4302.46	2 + 2.9959
3 + 2.9960	5.9960	3050.63	6	3049.08	3 + 2.9976
		3F		1F	
3.9990		6858.22	4	6857.76	3.9992
1 + 3.9989	4.9989	4389.00	5	4390.69	1 + 3.9980

Table 54. Part 1. Leading Levels of the First Band System

Curtis, 1929		Level	Venable, 1945	
Quantum No.	Wave No.		Wave No.	Quantum No.
1.788	34301.8	From 1S-mP		
		1S		
		From 1P-mS		
2.810	13893.1	2S	13901.24	2.8088
3.818	7524.6	3S	7532.74	3.8158
4.824	4713.3	4S	4721.44	4.8107
		From 1P-mS		
1.928	29517.2	1P	29525.39	1.9275
		From 1S-mP		
2.928	12795.4	2P		
3.928	7108.8	3P		
4.928	4516.3	4P		
		From 1P-z, x or D		
2.935	12734.	2Z	12742.14	
3.936	7080.	3Z	7088.14	
2.958	12533.	2X	12541.14	
3.013	12080.6	2D	12088.74	

Table 54. Part 2. Leading Levels of the Second Band System

Curtis, 1929		Level	Venable, 1945	
Quantum No.	Wave No.		Wave No.	Quantum No.
		From 1S-mP		
1.853	31958.1	1S		
		From 1P-mS		
2.873	13280.14	2S	13300.94	2.8715
		From 1P-mS		
1.904	28423.4	1P	28444.2	1.9635
		From 1S-mP		
2.904	12481.4	2P		
3.904	6978.5	3P		
4.904	4448.4	4P		
		From 1P-z, x or D		
2.503	12580.	2Z	12600.8	
2.072	12414.3	2X	12435.10	Hydrogen
3.018	12040.	2D	See text.	

Table 55. Rearrangement of Curtis' Band 2p-3d

<i>asbzbsaz</i>	28444.20	<i>azbzbsaz</i>	28444.20
<i>0azs</i>	12181.47	<i>3az</i>	12180.44
	16252.73		16257.76
Discrepancy	+ .14		+130.04
	16252.87	7	10393.80
		Discrepancy	- .15
			16393.05 6
Differences	Lines	Differences	Lines
+ 2.28 + 23.07	10318.22 2	- 1.51 + 6.02	10427.38 2
+ 2. + 21.00	204.25 4	- 1. + 8.11	420.70 3
+ 18.00	272.50 5	.76 + 9.11	412.65 3
Band head	10252.87 7	+ .80	403.54 4
- 18.96	233.91 8	- 0.50	384.00 5
- 18.37	215.54 5	+ .59 - 0.	375.06 6
- 18.53	197.01 5	+ 1.35 - 7.05	367.41 5
- 18.98	178.03 5	+ 2.27 0.38	362.03 2
- 10.84	158.10 2		
	16252.87 7		10252.87 7
	+ 54.16		+ 144.10
Discrepancy	10307.03		10307.03 4d
	- .58	- 5.02	301.11 4
	10306.45 2D	- 3.53 - 8.45	382.05 5
- 21.10	285.35 5	- 2.44 - 10.80	371.76 5
+ 3.88 - 17.22	268.13 0	+ 3.42 - 7.47	304.20 4
+ 4.18 - 13.04	255.09 5		
+ 3.53 - 90.51	245.08 7		Unclassified
+ 2.81 - 66.70	238.88 4	+ 45.04	10574.25 2
<i>bbbb-aabba</i>	136.04	+ 20.74	528.26 3
<i>bbbbb-abbbb</i>	54.16	+ 13.98	498.42 3
<i>ababa-aaaba</i>	? 144.16	+ 23.03	484.44 4
		+ 16.62	461.42 3
		+ 19.53	444.80 4
		+ 17.08	425.25 3
		+ 11.14	408.17 4
			16307.03 4d

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Table 56. Classification of Curtis' Doubtful Band

$a_2b_2ba_2$	28444.20	$a_2b_2ba_2$	28444.20
g_8a_2	6857.	g_8a_2	6858.22
	<u>21587.20</u>		<u>21585.98</u>
Discrepancy	+ .11	Discrepancy	- .57
Band head	21587.31	Band head	21585.41
	8		4
Differences	Lines	Differences	Lines
+ 9.97 + 54.32	21702.24 2	+ 29.99 + 62.53	21705.80 2
+ 8.09 + 34.35	647.92 4	+ 7.18 + 32.54	643.33 5
+ 26.26	613.57 10	+ 25.38	610.79 9
Band head	21587.31 8	Band head	21585.41 4
- 46.88	540.43 2	- 32.43	552.98 5
- 25.18	515.25 5	+ 11.45 - 20.98	532.00 2
- 30.35	484.90 2	+ 6.76 - 14.22	517.78 1
- 34.01	450.89 2		
$a_2b_2ba_2$	28444.20		Unclassified
$2a_2a_2a$	0860.17		21798.65 4
	<u>21578.03</u>		752.54 2
Null			752.46 3
+ 7.81 + 29.09	21661.66 2		733.51 2
+ 2.87 + 21.28	632.57 2		718.83
+ 3.16 + 16.23	618.57 10		712.06 2
+ 6.73 + 13.07	597.34 6		466.70 0
+ 6.24	21584.27 4		
Null	21578.03	The differences 54.32, 34.35, 26.26 and others in the table are readily identified with hydrogen differences in Table 1 of Chapter 2. The smaller differences are due to line molecules with six or more sub-atoms in line.	
- 3.29	574.74 2		
- 7.59 - 10.88	563.86 2		
- 10.40 - 21.28	542.58 2		
The line 21613.57 10 is a blend.			

Table 57. Reinterpretation of Dicke's Bands $2p-5'\delta\nu'$

P Branch			Q Branch			R Branch		
Null	24055.18 - 50.56	23995.42 2 993.52 1 930.70 1 800.46 0 881.23 1 824.67 1 788.84 0	a ₁ b ₂ b ₂ a ₂ 10a ₁		28444.20 4380.02	a ₂ b ₁ b ₁ a ₂ a ₃ a ₂		24844.20 4390.07
			Null	- 1.68	24055.18 053.50 6	Null	+ 25.78 + 24.11 + 22.24 + 20.19 + 18.30 + 16.23 + 13.00 + 10.35	24053.51 + 43.85
- .92	- 31.90	993.52 1	- 1.68	- 8.36	050.14 8	- 1.67	+ 25.78 + 24.11 + 22.24 + 20.19 + 18.30 + 16.23 + 13.00 + 10.35	24057.36 5 123.14 4
- .42	- 32.82	930.70 1	- 1.83	- 5.19	044.05 10	- 1.87	+ 22.24 + 20.19 + 18.30 + 16.23 + 13.00 + 10.35	147.25 4 169.49 3 186.68 3 207.98 2 224.21 2 237.81 3 248.16 2
- 1.99	- 35.23	881.23 1	- 1.54	- 6.63	038.32 5	- 2.05	+ 20.19 + 18.30 + 16.23 + 13.00 + 10.35	186.68 3 207.98 2 224.21 2 237.81 3 248.16 2
- 1.33	- 36.56	824.67 1	- 1.68	- 8.31	080.01 4	- 2.11	+ 18.30 + 16.23 + 13.00 + 10.35	207.98 2 224.21 2 237.81 3 248.16 2
+ .63	- 35.83	788.84 0	- 1.66	- 9.07	020.04 3	- 1.93	+ 16.23 + 13.00 + 10.35	224.21 2 237.81 3 248.16 2
			- 1.47	- 11.44	008.00 5	- 2.53	+ 13.00 + 10.35	
			- 1.74	- 13.18	23905.42 2	- 2.35	+ 10.35	
			- 1.55	- 14.73	080.00 1			
					24055.18 - 10.41			24097.25 5 - 10.14
					24044.77 - 59.81			24087.22 5
- 1.52	- 31.71	930.70 1	- 1.82	- 3.50	043.00 6	- 1.70	+ 25.44 + 23.74 + 22.05 + 19.90 + 18.14 + 15.28 + 14.45	112.66 6 136.40 6 158.45 5 178.54 5 196.68 4 211.96 2 220.41 1
	- 33.23	920.02 4	- 1.68	- 5.18	039.50 6	- 1.60	+ 22.05 + 20.34 + 18.65 + 16.95 + 15.25 + 13.55 + 11.85	136.40 6 158.45 5 178.54 5 196.68 4 211.96 2 220.41 1
			- 1.62	- 6.80	034.41 6	- 2.08	+ 19.90 + 18.14 + 16.45 + 14.75 + 13.05 + 11.35 + 9.65	158.45 5 178.54 5 196.68 4 211.96 2 220.41 1
					027.01 7	- 1.85	+ 18.14 + 16.45 + 14.75 + 13.05 + 11.35 + 9.65	178.54 5 196.68 4 211.96 2 220.41 1
59.56	bbbb-a-bbbba							24097.25 5
43.66	aaaaa-aaaaaa							- 31.34
32.	bbaaa-bbaab							24066.02 6
1.88	a ₁ a ₂ -a ₁ a ₂							088.07 7
1.77	a ₂ a ₃ -2a ₄ a ₂							100.80 6

Table 58

The Limit of the Regular Spectrum of Helium
Calculated from Kruger's Measurements

n	I	Line	Level	Limit
2	50	329186.8	100728.9	438015.7
3	30	300145.6	48708.2	438013.8
4	20	411481.3	27432.1	438013.38
5	15	421354.7	17550.44	438011.14
6	10	420720.0	12192.02	438012.02
7	7	420955.6	8057.41	438012.01
8	4	432054.8	6858.01	438012.81
9	2	433004.1	4518.07	438012.77
10	1	434523.8	4380.13	438012.03
11	0	435285.4	3026.38	438012.78

Kruger's wave numbers, calculated from measurements of the helium lines corresponding to the Lyman series in hydrogen are given in the third column; relative intensities to the left. The levels calculated by the simple Rydberg formula are given in the two columns to the right.

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Table 59. The o-S — mP Series

Lyman			Fowler	Sum	
λ	I	ν	mP		
584.40	10	171115.67	27175.17	108290.84	
537.12	7	180178.13	12100.56	108278.09	
522.21	5	191493.84	6817.21	108311.05	
515.65	4	193920.99	4307.45	108297.44	
512.09	3	195278.17	3035.05	108313.22	
510.05	2	196051.21	2230.52	108281.73	
508.59	1	196022.03	1708.40	108330.43	
Hopfield					
584.328	88	171136.7	27175.17	108301.87	
537.014	44	180214.9	12100.56	108315.40	
522.186	22	191502.6	6817.21	108310.81	
515.596	20.6	193950.3	4307.45	108317.75	
512.07	18.5	195286	3035.05	108321.05	
509.97	14.5	196000	2230.52	108320.52	
508.63	10	196607	1708.40	108315.40	
507.71	6	196963	1350.47	108313.40	
507.08	5.2	197208	1003.16	108301.16	
506.56	5	197410	903.38	108313.38	
Col. 1	Col. 2	Col. 3	Col. 4	Hydrogen Diff. Chapter 2	
Hopfield Line	From Table 3	Col. 1 + Col. 2	Col. 3 — 108313.10		
171136.7	27425.15	108561.85	248.06	baa-aaa Table 16 Table 6 Table 1	
180214.9	12188.12	198403.02	80.83		
191502.6	6855.58	198358.18	34.49		
193950.3	4387.48	198338.78	24.50		
Lyman's estimate of the series limit					
Kruger's estimate of the series limit					
Hopfield's estimate of the series limit					
Venable's estimate of the series limit					
198208					
108307					
108314.4 ± 5					
108313.10					

Table 60. Hopfield's Band
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Col. 1	Col. 2	Col. 3	Col. 4	Col. 6 Diff.
λ Hopfield	ν	Fowler	Col. 2 + Col. 3	
		20224		
722	138504	12746	151250	
694	144092	7093	151185	- 65
682	146027	4510	151137	- 42
675	148148	3118	151266	+ 120
671	149031	2283	151314	+ 48
669	149477	1744	151221	- 93
		Average	151220	

Table 61. Levels of the Helium Spectrum Due to Line Molecules Composed of Sub-atoms No. 2 Only, and First Order Levels Due to Accretions of Hydrogen Atoms in the *a*-Configuration

Molecule	Wave No.	Quantum No.
<i>c</i> ₁	637225.00	.415
<i>cac</i> ₂		
<i>cacac</i> ₃	38454.08	1.6889
<i>cacacac</i> ₂	15073.02	2.6974
<i>acacacac</i> ₂	8012.54	3.6999
<i>acacacacac</i> ₂	4903.67	4.7007
<i>acacacac</i> ₃	32032.30	1.8503
<i>aaacacac</i> ₂	13445.04	2.8560
<i>aaacacacac</i> ₂	7370.50	3.8575
<i>aaaacacacac</i> ₂	4147.22	4.8588
<i>bacacab</i> ₂	34301.8	1.788
<i>abacacab</i> ₂	13901.84	2.8088
<i>abacacab</i> ₃	7532.74	3.8158
<i>aabacacab</i> ₂	4721.44	4.8107
<i>bababab</i> ₂	29525.30	1.9273
<i>abababab</i> ₂	12705.4	2.928
<i>abababab</i> ₃	7108.8	3.928
<i>aabababab</i> ₂	4510.3	4.928
<i>asbbsbs</i> ₂	28444.2	1.9635
<i>aasbbsbs</i> ₂	12481.4	2.964
<i>aabbsbs</i> ₂	6978.5	3.964
<i>aaabbsbs</i> ₂	4448.4	4.964

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Table 62. Analysis of Levels of Li I

		Series $6\ zs'$	Lithium ms Q No.	Lithium ms Diff.	m
		43486.30 10280.5 8475.2 5187.8 3500.4 2535.6	1.5881 2.5055 3.5074 4.5079	1.0074 1.0019 1.0005	2 3 4 4
Helium		Diff.	a_6a_5	Lithium mp	
1.9635 2.964 3.964 4.964	28444.2 12481.4 0978.5 4448.4	138.3 79. 39.7 24.9	28582.5 12560.4 7018.2 4473.6	1.0588 2.0550 3.0532 4.0514 and 37 more terms	2 3 4 5
Helium			a_6a_3	Lithium md	
12205.78 6864.2 4880.		2.78 .7 .6	12203.1 0863.6 4389.6	and 4 more terms	
Helium			$a_2a_2a_2a_2$	Lithium m'	
6857.76			6856.1 4381.8		

Table 63. Analysis of the Levels of Na I

m	Diff.	Q No.	m_s				
3		1.6267	41449.00				
4	1.0158	2.6423	15709.50				
5	1.0042	3.6465	8248.28				
6	1.0012	4.6477	5077.31				
7	1.0010	5.6487	3427.28				
8	1.0000	6.6493	2480.06				
		and six others					
			$mp\frac{1}{2}$	Diff.	$mp\frac{1}{2}$	Q No.	Diff.
3		2.1161	24492.88	17.18	24475.65	2.1168	
4	1.0158	3.1319	11181.63	5.49	11176.14	3.1326	1.0149
5	1.0040	4.1368	6508.83	2.49	6408.34	4.1376	1.0049
6	1.0023	5.1301	4152.80	1.50	4151.30	5.1405	1.0029
7	1.0011	6.1402	2908.93	1.47	2907.46	6.1437	1.0032
8			2150.89	.89	2149.80		
9			1655.31	1.23	1654.08		
		and thirty-two singlet terms					
			md		mf		
3		2.9890	12276.18				
4	.0078	3.9808	6900.35				
5	.0088	4.9856	4412.47				
6	.0094	5.9850	3061.02				
7			2248.56				
8			1720.88				
9			1357.2				
		and six more terms					
3s is due to $6s_1$.				No differences due to hydrogen			
3p is due to $a2s_2a2s_2a2s$.				only are found. Probably substantially all hydrogen atoms are extensions of the line molecules necessary to provide levels for the long series, particularly the P levels.			
3p is due to $2a2s_2a2s_2a2s$.							
3d is due to $a2s_2a3s_2$.							
4f is due to $a2s_2a2s_2a2s$.							

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Table 64. Analysis of the s Levels of Ne I

1.5 S5 = <i>asizaa</i>				H Diff.	ms4	Q No.	Diff.
m	Diff.	Q No.	ms5				
1.5		1.6582	39887.61	417.45	39470.16	1.6609*	
2.5	1.0163	2.6745	15332.17	190.67	15141.50	2.6014	1.0245
3.2	1.0043	3.6788	8101.24	84.56	8016.98	3.6988	1.0074
4.5	1.0025	4.6813	5004.81	42.71	4982.10	4.7014	1.0026
and seven more terms				and seven more terms			
m	ms3	Diff.	ms5	Diff.	ms2		
1.5	39110.81	776.80	39887.61	1846.88	38040.73		
2.5	14554.05	777.12	15332.17	1035.80	14399.28		
3.5	7323.18	778.11	8101.24	828.28	7292.00		
4.5	4223.47	781.34	5004.81	803.00	4201.81		
5.5	2616.58	780.14	3398.71	791.20	2605.42		
6.5	1675.10	781.02	2456.10	788.45	1667.87		

1.5 s_3 is probably due to *asizaaa'zaa*.

1.5 s_2 is probably due to *asizaa'za'a*.

The other levels arise because of hydrogen accretions.

417.45 Compare 418.33 due to *bbbb-aaaa*.

190.67 is not known with accuracy because the levels 2.5 s were obtained by interpolation and not from observed lines, which would be in the infrared.

84.56 Compare with 84.35 due to *bbbab-abbab*.

42.71 Compare with 43.86 due to *baaaa-aaaaaa*.

Table 65. Analysis of the p Levels of Ne II

3p10 $a_2x_3z_2$			mp 10	H	mp 9	Q. No.	Diff.
m	Diff.	Q. No.	Wave No.	Diff.	Wave No.		
3		2.0069	25071.65	1300.24	24202.41	2.0460	
4	1.0383	3.1002	11411.49	312.77	11008.78	3.1430	1.0970
5	1.0130	4.1141	0479.93	100.04	6370.20	4.1495	1.0050
6	1.0075	5.1216	4181.24	49.01	4132.28	5.1519	1.0024
7	1.0070	6.1286	2920.00	23.55	2806.54	6.1535	1.0016
2p8 $b_2x_3z_2$			mp 8	H	mp 7		
3		2.1336	24105.23	297.38	23807.85	2.1463	
4	1.0197	3.1523	11030.29	113.51	10016.78	3.1608	1.0125
5	1.0066	4.1509	0383.19	48.34	6280.81	4.1760	1.0061
6	1.0020	5.1028	4114.71	24.76	4080.95	5.1784	1.0025
7	1.0021	6.1040	2835.75	14.21	2871.44	6.1803	1.0019
3p6 a_2x_3z			mp 6	Diff.	mp 3	3p3	$a_2x_3z_2$
3		2.1551	23618.59	601.57	28012.02	2.1831	
4	1.0340	3.1801	10801.04	372.05	10528.00	3.2276	1.0445
5	.9807	4.1788	6280.71	218.56	6002.15	4.2635	1.0250
6	.9841	5.1020	4085.50	132.04	3952.05	5.2676	1.0141
7	1.0100	6.1820	2860.15	88.64	2780.81	6.2803	1.0137
3p5 $b_2x_3z_2x_3'z_2$			mp 5	H	mp 4		
3			23157.34	126.40	23074.04		
4			10273.13	51.31	10220.82		
5			5573.00	23.25	5550.65		
6			3344.40	12.31	3332.15		
7			2107.1	5.7	2101.4		
3p2 $a_2x_3z_2x_3'z_2$			mp 2	Diff.	mp 1	3p1 $a_2x_3z_2x_3'z_2$	
3			22891.00	1032.28	20058.72		
4			10221.60	578.18	9643.51		
5			5570.75	228.31	5342.44		
6			3350.98	110.04	3240.04		
7			2120.25	110.30	2015.05		

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Table 66. Analysis of the d Levels of Ne I

m	Diff.	Q. No.	md _{1'}	Diff.	md _{1''}	Q. No.	Diff.
3		2.9041	12228.05	1.70	12229.81	2.9047	
4	.9983	3.9924	6880.70	1.01	6881.86	3.9934	.0087
5	.9988	4.9912	4402.56	.60	4403.16	4.9910	.0085
6			3056.20	.42	3056.62		
7			2243.92	.20	2244.12		
			md ₄		md ₄		
3		2.9816	12337.32	1.83	12339.16	2.9814	
4	.9971	3.9787	6928.27	1.00	6929.46	3.9784	.0070
5	.9989	4.9776	4427.15	.02	4427.77	4.9770	.0080
6			3070.55	.41	3070.06		
7			2253.70	.31	2254.01		
			md ₅		md ₅		
3		2.9870	12292.85	29.41	12322.26	2.9834	
4	.9992	3.9862	6902.48	15.44	6917.02	3.9817	.0083
5	.0004	4.9866	4412.44	8.45	4420.89	4.9808	.0091
6			3061.51	5.15	3066.46		
			2240.58	1.53	2248.11		
			md ₆		md ₆		
3		2.9734	12405.23	14.64	12419.87	2.9717	
4	.9980	3.9714	6954.13	7.67	6961.80	3.9693	.0070
5	.9981	4.9695	4441.03	5.41	4446.44	4.9665	.0072
6			3078.13	3.11	3081.24		
7			2257.52	2.75	2248.11		
		md ₂	Diff.	ms _{1'}	Diff.	ms _{1''}	Diff.
3	12292.85	799.07	11193.78	15.72	11509.50	812.76	12322.26
4	6902.48	781.19	6121.29	11.21	6132.50	785.42	6917.02
5	4412.44	779.01	3633.47	6.68	3640.11	780.78	4420.89
6	3061.51	770.05	2284.56	2.73	2287.20	770.17	3066.46
7	2240.58	778.18	1468.40	2.60	1471.00	777.11	2248.11
		md ₅	Diff.	ms _{1'''}	Diff.	ms _{1''''}	Diff.
3	12405.23	885.07	11510.26	.50	11520.82	890.05	12410.47
4	6954.13	820.57	6133.56	.01	6134.47	827.33	6901.80
5	4441.03	801.28	3639.75	.72	3640.47	805.07	4440.44
6	3078.13	791.10	2287.02	2.43	2289.45	791.17	3081.24
7	2257.52	786.70	1470.82	.73	1471.00	788.72	2260.27
$3d_1' = 2a_5^2a_4^2a_2$		$3d_3 = ab^2a_4^2x_3a_3ba_2$		$3s_1' = a_2b^2a_3x_3x_3^2x_3^2a_2a_2$		$3d_1'' = a_2a_2^2a_3a_2a_2$	
$3d_1'' = a_2a_2^2a_3a_2a_2$		$3d_3 = ab^2a_4^2x_3a_3b_1$		$3s_1'' = ab_2x_3x_3x_3x_3a_2b_2$		$3d_3 = 2a_2a_2^2a_3x_3x_3a_2a_2$	
$3d_4 = 2a_2a_2^2a_2x_2a_2a_2$		$3d_5 = 2a_2a_2^2a_4x_2a_2a_2$		$3s_1''' = a_2a_2a_2x_3x_3x_3a_2a_2$		$3d_4' = a_2a_2a_2^2a_2x_2a_2a_2$	
$3d_4' = a_2a_2a_2^2a_2x_2a_2a_2$		$3d_6 = a_2a_2a_2^2a_4x_2a_2a_2$		$3s_1'''' = a_2a_2a_2x_3x_3x_3x_3a_2a_2$			

Table 67. Analysis of Wave Numbers of Levels of Li II

$$\begin{array}{c} 1S \\ C_2 - 4a_1 \\ 610112 = 637543 - 27431 \end{array}$$

3S					1S				
n	Wave No.	Q. No.	Diff.	Molecule	Wave No.	Q. No.	Diff.	Molecule	
2	134033	.9048		$a_1^2 x_1'$	51300	1.4622			
3	55318	1.4085	.8039	$a_2 x_1' a_3$	28448	1.9621	.4999	$a_2 a_3 x_1' x_2' a_3$	
4	30097	1.9095	.5010		18095	2.4619	.4998		
5	18865	2.4100	.5005		12805	2.9615	.4996		
6	12959	2.0094	.4994		9154	3.4539	.4924		
7	9438	3.4080	.4995						
3P°									
n	Wave No.	Add H	Term	Q. No.	Molecule	Hydrogen difference			
2	115806	2467.75	118274	.983	$b_2 b_1$	2467.75 = 4a-5a			
3	50578	697.29	51278	1.483	$a_2 b_2 b_1$	697.29 = aaaa-aab			
4	28187	257.2	28444	1.9635	$a_2 b_2 b_2 a_2$	257.2 = baaa-aaab			
5	17938	143.34	18081						
6	12413	76.	12398						
1P°									
n	Wave No.	Add	Term	Q. No.	Molecule	Hydrogen difference			
2	108264	1459.22	109723	.999	$a_2 a_2$	436.68 = abab-bbb			
3	48330	425.87	48765	1.499	$a_2 a_2 a_2$				
4	27245	185.80	27430		$a_2 a_2 a_2 a_2$				
5	17440	115.71	17655						

The D and F levels are separated from some of the levels of Table 52 by small hydrogen differences. Some corrections may be necessary when more accurate data are available.

TABLES OF DATA

Table 68

	n	$1 - \frac{1}{n^2}$	$\frac{1}{2^2} - \frac{1}{n^2}$	$\frac{1}{3^2} - \frac{1}{n^2}$	$\frac{1}{4^2} - \frac{1}{n^2}$	$\frac{1}{5^2} - \frac{1}{n^2}$	$\frac{1}{6^2} - \frac{1}{n^2}$
Sub. 1	1	1.					
	2	.25	.75				
	3	.111	.889	.139			
	4	.062	.938	.188	.049		
	5	.04	.96	.21	.072	.023	
	6	.028	.972	.222	.083	.034	.011
Sub. 2	1	4.					
	2	1.	3.				
	3	.444	3.556	.556			
	4	.25	3.75	.75	.194		
	5	.18	3.84	.84	.284	.09	
	6	.111	3.889	.889	.333	.139	.049
Sub. 3	1	9.					
	2	2.25	6.75				
	3	1.	8.	1.25			
	4	.562	8.437	1.687	.437		
	5	.38	8.04	1.89	.64	.203	
	6	.25	8.75	2.	.75	.313	.11
Sub. 4	1	16.					
	2	4.	12.				
	3	1.778	14.222	2.222			
	4	1.	15.	3.	.778		
	5	.64	15.36	3.36	1.138	.36	
	6	.444	15.556	3.556	1.334	.556	.196
Sub. 5	1	25.					
	2	6.25	18.75				
	3	2.777	22.223	3.473			
	4	1.562	23.438	4.088	1.215		
	5	1.	24.	5.25	1.777	.562	
	6	.694	24.306	5.556	2.073	.808	.306

Table 69. K X-Ray Lines and Differences from Line to Line

	11 Na		12 Mg		13 Al		14 Si		15 P	
	Line	Diff.	Line	Diff.	Line	Diff.	Line	Diff.	Line	Diff.
β'''					116.09		137.05		160.46	
β''					116.55	.44	137.28	.67	169.87	.59
β_5										
β''										
β_2	78.88		95.02		114.71	1.84	135.22	2.06	157.67	2.20
β_{12}										
β_1	78.00	-.28	95.53	.39	114.41	.30	134.01	.31	157.44	.28
β'	77.86	-.74	94.45	1.08	113.30	1.11	134.12	.79	157.33	.11
α_6	77.96	+.10	93.89	.56	111.27	2.03	130.11	4.02	156.57	.76
α_5	77.76	.20	93.65	.24	111.00	.27	129.90	.21	150.40	6.17
α_4	77.31	.45	93.12	.53	110.44	.56	120.10	.74	149.49	.91
α_3	77.19	.12	92.07	.15	110.23	.21	128.90	.17	149.32	.17
α'	76.08	.21	92.74	.23	109.97	.26	128.64	.35	148.98	.34
α_1										
α_2	76.67	.31	92.34	.40	109.52	.45	128.15	.49	148.35	.63

	16 S		17 Cl		19 K		20 Ca		21 Sc	
	Line	Diff.								
β'''					268.31		290.75			
β''	184.45		210.63		267.67	.64	299.01	.74	332.38	
β_5					265.33	2.34	297.02	1.00	330.41	
β''					264.67	.66	295.90	1.12	329.28	
β_2	181.79	2.65	207.55	3.08						
β_{12}	181.61	.18	207.42	.13						
β_1	181.49	.12	207.38	.04	264.38	.20	205.54	.36	328.52	.76
β'	180.64	.85	206.83	.55			204.80	.74	325.55	2.97
α_6										
α_5	172.52	8.11								
α_4	171.19	1.34	194.55	12.28	245.70	18.68	273.65	21.15		
α_3	170.99	.20	194.38	.17	245.56	.14	273.47	.18	303.15	22.40
α'	170.63	.36	193.78	.60	245.05	.51	272.85	.62		
α_2	169.97	.66	193.14	.64	244.07	.98	271.88	.97	301.24	1.01
α_1	169.90	.07	193.02	.12	243.85	.22	271.62	.26	300.91	.38

TABLES OF DATA

Table 70 — Sheet 1

11 Na

β_x	β_1	β'	α_6	α_5	α_4	α_3	α'	$\alpha_{1,1}$
78.88	78.60	77.86	77.96	77.76	77.31	77.19	76.98	76.67
.75	.89	.89	.94	.94	.94	.97	.97	.97
.75	.89	.89	.89	.89	.94	.94	.96	.97
.75	.75	.75	.75	.75	.75	.75	.94	.96
.75	.75	.75						
81.88	81.88	81.14	80.64	80.34	79.94	79.85	79.85	79.57
3.	3.	3.75	3.55	3.75	3.75	3.84	3.84	3.89
			3.55	3.55	3.75	3.75	3.75	3.89
			3.55	3.55	3.75	3.75	3.75	3.84
84.88	84.88	84.89	91.19	91.19	91.19	91.19	91.19	91.19
8.44	8.44	8.44						
8.	8.	8.						
6.75	6.75	6.75						
108.07	108.07	108.08						

12 Mg

β_x	β_1	β'	α_6	α_5	α_4	α_3	α'	$\alpha_{1,1}$
95.92	95.53	94.45	93.89	93.65	93.12	92.07	92.74	92.34
.75	.94	.94	.75	.94	.75	.89	.92	.92
.75	.94	.94	.89	.94	.91	.92	.92	.89
97.42	97.41	96.33	95.53	95.53	94.78	94.78	94.58	94.15
3.75	3.75	3.75	3.55	3.55	3.75	3.75	3.75	3.89
3.55	3.55	3.55	3.55	3.55	3.55	3.55	3.75	3.84
3.	3.	3.	3.	3.	3.55	3.55	3.55	3.75
8.	8.	8.	8.	8.	3.	3.	3.	3.
8.	8.	8.	8.	8.	8.	8.	8.	8.
104.72	104.71	103.63	108.63	108.63	108.63	108.63	108.63	108.63
8.	8.	8.04						
8.	8.	8.44						
8.	8.	8.						
128.72	128.71	128.71						

13 Al

β'''	β'''	β_x	β_1	β'	α_6	α_5	α_4	α_3	α'	$\alpha_{1,1}$
116.09	110.55	114.71	114.41	113.30	111.27	111.00	110.44	110.23	109.97	100.52
3.75	3.75	3.89	3.80	3.89	3.84	3.91	3.84	3.84	3.91	
3.	3.	3.	3.	3.55	3.55	3.75	3.84	3.84	3.89	3.84
3.	3.	3.	3.	3.55	3.	3.	3.55	3.75	3.89	3.84
3.	3.	3.	3.	3.	3.	3.	3.	3.	3.	3.55
120.74	120.30	127.60	127.30	127.29	127.66	127.66	127.66	127.66	127.66	127.66
8.	8.44	8.44	8.75	8.75						
6.75	6.75	8.44	8.44	8.44						
6.75	6.75	6.75	6.75	6.75						
151.24	151.24	151.23	151.24	151.23						

TABLES OF DATA

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Table 70 — Sheet 2

14 Si

β''''	β'''	β_x	β_1	β'	α_8	α_8	α_4	α_3	α'	$\alpha_{3,1}$
137.95	137.28	135.22	134.91	134.12	130.11	120.90	129.10	128.99	128.04	128.15
3.80	3.91	3.89	3.89	3.89	3.55	3.75	3.75	3.91	3.91	3.89
3.89	3.89	3.89	3.89	3.89	3.55	3.75	3.75	3.91	3.91	3.89
3.75	3.75	3.84	3.84	3.80	3.	3.	3.55	3.55	3.75	3.84
3.	3.	3.	3.	3.75						
152.48	151.83	149.84	149.53	149.54	140.21	140.20	140.21	140.20	140.21	139.77
8.44	8.64	8.75	8.75	8.75	8.	8.	8.	8.	8.	8.44
8.	8.44	8.04	8.75	8.75						
8.75	8.75	8.44	8.04	8.04						
175.07	175.00	175.07	175.07	175.08	148.21	148.20	148.21	148.20	148.21	148.21

15 P

β''''	β'''	β_x	β_1	β_{1x}	β'	$\alpha_{8,5}$	α_4	α_3	α'	$\alpha_{3,1}$
100.46	159.87	187.67	157.44	157.33	150.57	150.40	149.49	149.32	148.98	148.35
						.94	.94	.98	.96	.94
						.75	.75	.80	.80	.80
3.89	3.89	3.91	3.89	3.91	3.89	152.00	151.18	151.20	150.83	150.18
3.84	3.89	3.84	3.89	3.89	3.89	3.75	3.91	3.89	3.92	3.89
3.75	3.75	3.75	3.75	3.84	3.84	3.55	3.75	3.75	3.89	3.84
3.	3.55	3.55	3.75	3.75	3.75	3.	3.55	3.55	3.75	3.84
3.	3.	3.	3.	3.	3.					
177.04	177.95	175.72	175.72	175.72	174.00	102.30	162.30	162.30	162.30	161.75
12.	12.	12.	12.	12.	12.	8.	8.	8.	8.	8.64
12.	12.	14.22	14.22	14.22	15.	170.30	170.39	170.30	170.39	170.39
201.04	201.05	201.04	201.04	201.04	201.04					

16 S

β''''	β_x	β_{1x}	β_1	β'	$\alpha_{8,5}$	α_4	α_3	α'	α_1	α_3
184.45	181.70	181.61	181.49	180.04	172.52	171.10	170.00	170.03	160.07	160.00
					.75	.75	.75	.80	.80	.94
3.91	3.01	3.80	3.92	3.92	173.27	171.04	171.74	171.52	170.86	170.84
3.75	3.75	3.75	3.84	3.91		3.84	3.84	3.84	3.89	3.81
3.	3.	3.	3.	3.		3.75	3.84	3.84	3.89	3.80
						3.55	3.55	3.75	3.84	3.80
						3.	3.	3.	3.	3.
195.11	192.45	192.25	192.25	191.47	187.41	180.47	186.17	186.16	185.63	185.53
8.	8.44	8.64	8.64	8.64	6.75	8.	8.	8.	8.64	8.64
203.11	200.80	200.89	200.80	200.11	194.16	194.17	194.17	194.16	194.17	194.17
12.	14.22	14.22	14.22	15.						
15.	15.	15.	15.	15.						
230.11	230.11	230.11	230.11	230.11						

TABLES OF DATA

Table 70 — Sheet 3

17 Cl

β'''	β''	β_{12}	β_1	β'	α_4	α_3	α'	α_1	α_2
210.63	207.55	207.42	207.38	206.83	194.55 .94 .75	194.38 .07 .89	193.78 .94 .89	193.14 .94 .89	193.02 .94 .89
3.01	3.89	3.89	3.91	3.91	196.24 3.75 3.55	196.24 3.75 3.55	195.61 3.75 3.55	194.97 3.75 3.75	194.85 3.75 3.75
3.84	3.84	3.89	3.91	3.89					
3.75	3.84	3.84	3.84	3.84					
3.75	3.75	3.84	3.84	3.84					
3.75	3.75	3.75	3.75	3.75					
3.55	3.55	3.55	3.55	3.75					
233.18	230.17	230.18	230.18	229.82					
15.	15.	15.	15.	15.36	8. 8.	8. 8.	8.04 8. 8.44	8.04 8. 8.44	8.75 8. 8.44
12.	15.	15.	15.	15.					
260.18	260.17	260.18	260.18	260.18	219.54	219.54	219.55	219.55	210.54

19 K

β''''	β'''	β_3	β''	β_1	α_4	α_3	α'	α_1	α_2
268.31	267.67	265.33	264.67	264.38	245.70 .94 .75	245.50 .04 .80	245.05 .80	244.07 .80 .89	243.85 .80 .75
3.89	3.89	3.89	3.91	3.91	247.39 3.75 3.75	247.30 3.75 3.75	240.83 3.75 3.75	245.85 3.75 3.75	245.40 3.75 3.75
3.55	3.55	3.55	3.55	3.84	3. 3. 3.	3. 3. 3.	3.55 3. 3.	3.75 3. 3.	3.75 3. 3.
275.75	275.11	272.77	272.13	272.13	260.80	260.80	260.88	260.10	250.74
8.	8.04	8.75	8.75	8.75					
8.	8.	8.	8.64	8.64					
8.	8.	8.	8.	8.					
200.75	200.75	207.52	207.52	207.52					
14.22	14.22	14.22	14.22	14.22	14.22	14.22	14.22	15.	15.36
12.	12.	14.22	14.22	14.22					
325.07	325.07	325.00	325.00	325.00	275.11	275.11	275.10	275.10	275.10

Table 70 — Sheet 4

20 Ca

β''''	β'''	β_5	β''	β_1	β'	α_1	α_2	α'	α_1	α_2
299.75	299.01	297.02	295.00	295.54	294.80	273.05 .89 .89	273.47 .04 .04	272.85 .89 .94	271.88 .94 .94	271.62 .94 .94
3.55	3.75	3.84	3.84	3.84	3.84	275.43 3.89 3.75	275.33 3.89 3.84	274.68 3.01 3.84	273.70 3.89 3.89	273.50 3.84 3.84
3.	3.55	3.75	3.75	3.75	3.75					
3.	3.	3.	3.	3.	3.					
300.30	300.31	307.61	306.40	306.13	305.10	283.07 8.	283.08 8.	282.43 8.64	281.54 8.75	281.18 8.75
8.44	8.44	8.44	8.44	8.44	8.75					
8.	8.	8.	8.	8.	8.44					
6.75	6.75	8.	8.	8.	8.44					
332.40	332.50	332.40	331.37	331.01	331.02	201.07 14.22	291.08 14.22	201.07 14.22	290.20 15.	280.93 15.36
15.	15.	15.	15.30	15.30	15.30					
14.22	14.22	14.22	15.	15.36	15.30					
301.71	301.72	301.71	301.73	301.73	301.74	305.20	305.30	305.20	305.20	305.29

21 Sc

β'''	β_5	β''	β_1	β'	$\alpha_{1,2}$	α_1	α_2
332.28	330.41	329.28	328.52	325.55	303.15	301.24	300.91
3.80	3.80	3.80	3.80	3.80	3.01	3.91	3.02
3.84	3.84	3.80	3.80	3.84	3.80	3.91	3.80
3.75	3.75	3.84	3.84	3.84	3.84	3.84	3.80
					3.55	3.55	3.84
343.70	341.80	340.00	340.14	337.12	318.34	316.35	310.35
8.44	8.04	8.04	8.04	8.04	0.75	8.64	8.04
0.75	8.44	8.04	8.04	8.04			
358.05	358.97	358.18	357.42	354.40	325.00	325.00	325.00
14.22	14.22	15.	15.	15.	12.	12.	12.
14.22	14.22	14.22	15.	15.			
12.	12.	12.	12.	15.			
300.30	300.41	300.40	300.42	300.40	337.00	337.00	337.00

TABLES OF DATA

Table 70 — Sheet 5

22 Ti

β_3	β_5	β''	β_1	β'	α_i, z	α_1	α_3
366.91	365.43	364.41	363.20	362.05	334.18	332.20	331.76
3.75	3.89	3.84	3.91	3.84	3.91	3.89	3.89
3.	3.55	3.84	3.84	3.84	3.84	3.84	3.84
					3.55	3.55	3.55
					3.55	3.55	3.55
373.66	372.87	372.09	370.95	369.78	349.03	347.03	346.59
8.44	8.	8.	8.	8.64	8.	8.75	8.75
6.75	8.	8.	8.	8.	6.75	8.	8.44
6.75	6.75	6.75	6.75	6.75	6.75	6.75	6.75
395.60	395.62	394.84	393.70	393.12	370.53	370.53	370.53
15.	15.	15.	15.36	15.36			
14.22	14.22	14.22	15.	15.			
14.22	14.22	14.22	15.	15.			
439.04	439.06	439.06	439.06	439.04			

23 V

β'''	β_3	β''	β_1	β'	η	α_i, z	α_1	α_3
403.63	402.34	400.98	399.73	398.32	394.03	366.77	304.75	304.20
3.84	3.89	3.91	3.91	3.91	3.91	3.89	3.01	3.91
3.84	3.84	3.84	3.84	3.91	3.89	3.55	3.55	3.55
411.31	410.07	408.73	407.48	406.14	401.83	374.21	372.21	371.66
8.64	8.64	8.64	8.64	8.64	8.82	8.64	8.75	8.75
6.75	8.	8.	8.	8.	8.44	8.	8.84	8.75
6.75	6.75	6.75	8.	8.	8.	8.	8.	8.44
6.75						6.75	8.	8.
433.46	433.46	432.12	432.12	430.78	427.09	405.60	405.60	405.60
14.22	14.22	14.22	14.22	15.56	15.87			
14.22	14.22	15.56	15.56	15.56	15.56			
461.89	461.90	461.90	461.90	461.90	458.32			
18.75	18.75	18.75	18.75	18.75	22.33			
480.64	480.65	480.65	480.65	480.65	480.65			

Table 70 — Sheet 6

24 Cr

β'''	β_5	β''	β_1	β'	η	$\alpha_{3, 4}$	α_1	α_2
442.00	440.93	430.59	437.98	436.91	431.55	400.86	398.80	398.12
3.55	3.55	3.75	3.75	3.75	3.84			
3.55	3.55	3.65	3.75	3.75	3.84			
449.10	448.03	446.89	446.48	444.41	439.23			
8.	8.64	8.82	8.64	8.89	8.82	8.	8.82	8.86
8.	8.44	8.64	8.75	8.82	8.82	6.75	8.	8.64
465.10	465.11	464.35	462.89	462.12	466.87	415.61	415.62	415.62
14.22	14.22	15.	14.22	15.	15.56			
14.22	14.22	14.22	14.22	14.22	14.22			
12.	12.	12.	14.22	14.22	14.22			
505.54	505.55	505.57	505.55	505.56	500.87			
18.75	18.75	18.75	18.75	18.75	23.44			
524.29	524.30	524.32	524.30	524.31	524.31			

25 Mn

β'''	β_5	β_1	β'	$\alpha_{3, 4}$	α_1	α_2
482.46	481.32	478.00	476.98	436.45	434.45	433.63
8.	8.	8.75	8.75	8.	8.	8.82
6.75	6.75	8.	8.04	6.75	8.75	8.75
6.75	6.75	8.	8.44			
503.98	502.82	502.81	502.81	451.20	451.20	451.20
14.22	15.36	15.36	15.36			
518.18	518.18	518.17	518.17			
18.75						
18.75						
14.22						
569.90						

26 Fe

β'''	β_5	β''	β_1	β'	η	$\alpha_{4, 2}$	α_1	α_2
524.33	523.48	522.22	510.83	518.81	512.04	473.81	471.65	470.64
8.44	8.86	8.86	8.86	8.86	8.86	8.75	8.82	8.82
8.	8.44	8.44	8.44	8.44	8.82	8.75	8.82	8.82
6.75	6.75	8.	8.	8.64	8.82	8.	8.75	8.75
6.75	6.75	6.75	8.	8.	8.64	0.75	8.	8.64
554.27	554.28	554.27	553.13	553.13	547.18	500.06	506.04	505.67
14.22	14.22	14.22	15.36	15.36	15.36	15.	15.	15.36
568.49	568.50	568.49	568.49	568.49	502.54	521.00	521.04	521.03
18.75					23.44			
23.44					23.44			
610.68					609.42			
6.75					8.			
617.43					617.43			

TABLES OF DATA

Table 71

First Lyman Line					Second Lyman Line				
No.	Diff.	Diff.	$\frac{1}{2}n^2$	n^2	n^2	$\frac{1}{2}n^2$	Diff.	Diff.	No.
8			48.34	64.45	64.45	57.08			8
9		12.66	61.13	81.51	81.48	72.35	14.20		9
10	1.58	14.24	75.37	100.49	100.49	89.33	16.98	1.60	10
11	1.58	15.82	91.19	121.50	121.50	108.08	18.75	1.77	11
12	1.60	17.42	108.01	144.81	144.81	128.72	20.04	1.80	12
13	1.58	19.00	127.61	170.15	170.15	151.24	22.52	1.88	13
14	1.60	20.00	148.21	197.61	197.61	175.07	24.43	1.91	14
15	1.58	22.18	170.39	227.19	227.18	201.94	26.20	1.88	15
16	1.60	23.75	194.17	258.89	258.87	230.11	28.17	1.88	16
17	1.58	25.37	210.54	292.72	292.70	280.18	30.07	1.90	17
18	1.60	26.09	246.53	328.71	328.65	292.13	31.95	1.89	18
19	1.50	28.58	275.11	386.81	386.73	325.97	33.84	1.89	19
20	1.60	30.18	305.20	407.05	406.95	381.73	35.70	1.02	20
21	1.02	31.80	327.09	419.45	449.33	390.40	37.00	1.03	21
22	1.64	33.44	370.53	494.04	493.02	430.04	39.64	1.95	22
23	1.03	35.07	405.60	540.80	540.73	480.05	41.07	1.07	23
24					589.55	524.31	43.66	1.95	24
25					641.14	588.00	45.60	1.03	25
26					694.81	617.43	47.53	1.94	26

Table 72. Analysis of L X-Ray Lines

23 V	24 Cr		25 Mn		26 Fe				
	L ₃ -M ₄	L ₃ -M ₁	L ₃ -M ₁	L ₃ -M ₄	L ₃ -M ₄	L ₃ -M ₁			
37.70	42.30	43.	47.	48.	45.3	46.4	51.8	52.0	54.8
3.	3.55	3.	3.	8.	3.	3.	3.55	3.	3.
3.75	3.55	3.55	3.55	3.	3.	3.75	3.55	3.	3.
3.84	3.75	3.55	3.75	3.55	3.		8.	8.	3.55
			3.84	8.55	3.84	8.	8.44	8.44	8.
48.20	61.15	61.10	61.14	61.10	61.14	61.15	75.34	75.34	75.35

27 Co						28 Ni		
L ₃ -M ₁	L ₃ -M ₁	L ₃ -M ₄	L ₃ -M ₄	L ₃ -M ₁	L ₃ -M ₁	L ₃ -M ₄	L ₃ -M ₄	L ₃ -M ₃
50.1	51.3	57.2	58.3	55.1	50.4	62.7	64.0	60.36
3.	3.	3.55	3.	3.55	3.	3.55	3.	3.
3.55	3.75	3.55	3.55			3.75	3.	3.55
3.55	3.84	3.55	3.75			3.89	3.80	3.55
6.75	6.75	3.75		8.	8.	8.44	8.44	3.75
8.44	6.75	3.75	6.75	8.75	8.	8.86	8.86	8.
75.39	75.39	75.35	75.35	75.40	75.40	91.10	91.10	91.21

20 Cu							30 Zn		
L ₃ -M ₁	L ₃ -M ₁	L ₃ -M ₄	L ₃ -M ₄	L ₁ -M ₃	L ₃ -M ₁	L ₃ -M ₁	L ₃ -M ₄	L ₃ -M ₄	L ₁ -M ₃
60.0	61.5	68.6	69.94	75.3	65.3	67.0	74.51	76.2	81.7
3.	3.	3.55	3.	3.	3.	3.	3.55	3.55	3.55
3.75	3.	3.55	3.	3.	3.84	3.84	3.55	3.55	3.55
3.75	3.	3.84	3.55	3.55			3.84	3.84	3.84
3.84	3.84	3.89	3.84	3.84	8.	6.75	3.89	3.84	3.89
		8.	8.	3.89	8.	8.75	6.75	6.75	8.
8.	8.	8.44	8.44	8.	8.44	8.	8.44	6.75	8.86
8.86	8.86	8.82	8.82	8.	12.	12.	8.86	8.86	8.86
91.20	91.20	108.59	108.59	108.58	108.58	108.59	127.61	127.61	127.61

Table 73. Classification Levels and Molecular Limits in Hydrogen

Differences	Molecular limit	Mole-	Classifica-	Differences
	117754.43 100078.	<i>b</i> <i>a</i>	117754.43 109078.	8076.43
	82370.15 88427.01 82258.50	<i>ba</i> <i>bb</i> <i>aa</i> <i>ab</i>	85375.27 20326.52 27410.50	1907.02
17 22 23 3 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 53 54 55 56 57 58 59 60 61 62 63 64 65 66 67 68 69 70 71 72 73 74 75 76 77 78 79 80 81 82 83 84 85 86 87 88 89 90 91 92 93 94 95 96 97 98 99 100 101 102 103 104 105 106 107 108 109 110 111 112 113 114 115 116 117 118 119 120 121 122 123 124 125 126 127 128 129 130 131 132 133 134 135 136 137 138 139 140 141 142 143 144 145 146 147 148 149 150 151 152 153 154 155 156 157 158 159 160 161 162 163 164 165 166 167 168 169 170 171 172 173 174 175 176 177 178 179 180 181 182 183 184 185 186 187 188 189 190 191 192 193 194 195 196 197 198 199 200 201 202 203 204 205 206 207 208 209 210 211 212 213 214 215 216 217 218 219 220 221 222 223 224 225 226 227 228 229 230 231 232 233 234 235 236 237 238 239 240 241 242 243 244 245 246 247 248 249 250 251 252 253 254 255 256 257 258 259 260 261 262 263 264 265 266 267 268 269 260 261 262 263 264 265 266 267 268 269 270 271 272 273 274 275 276 277 278 279 270 271 272 273 274 275 276 277 278 279 280 281 282 283 284 285 286 287 288 289 280 281 282 283 284 285 286 287 288 289 290 291 292 293 294 295 296 297 298 299 290 291 292 293 294 295 296 297 298 299 300 301 302 303 304 305 306 307 308 309 310 311 312 313 314 315 316 317 318 319 320 321 322 323 324 325 326 327 328 329 330 331 332 333 334 335 336 337 338 339 340 341 342 343 344 345 346 347 348 349 350 351 352 353 354 355 356 357 358 359 360 361 362 363 364 365 366 367 368 369 360 361 362 363 364 365 366 367 368 369 370 371 372 373 374 375 376 377 378 379 380 381 382 383 384 385 386 387 388 389 380 381 382 383 384 385 386 387 388 389 390 391 392 393 394 395 396 397 398 399 390 391 392 393 394 395 396 397 398 399 400 401 402 403 404 405 406 407 408 409 410 411 412 413 414 415 416 417 418 419 420 421 422 423 424 425 426 427 428 429 420 421 422 423 424 425 426 427 428 429 430 431 432 433 434 435 436 437 438 439 440 441 442 443 444 445 446 447 448 449 440 441 442 443 444 445 446 447 448 449 450 451 452 453 454 455 456 457 458 459 460 461 462 463 464 465 466 467 468 469 460 461 462 463 464 465 466 467 468 469 470 471 472 473 474 475 476 477 478 479 480 481 482 483 484 485 486 487 488 489 480 481 482 483 484 485 486 487 488 489 490 491 492 493 494 495 496 497 498 499 490 491 492 493 494 495 496 497 498 499 500 501 502 503 504 505 506 507 508 509 510 511 512 513 514 515 516 517 518 519 520 521 522 523 524 525 526 527 528 529 530 531 532 533 534 535 536 537 538 539 540 541 542 543 544 545 546 547 548 549 540 541 542 543 544 545 546 547 548 549 550 551 552 553 554 555 556 557 558 559 560 561 562 563 564 565 566 567 568 569 560 561 562 563 564 565 566 567 568 569 570 571 572 573 574 575 576 577 578 579 580 581 582 583 584 585 586 587 588 589 580 581 582 583 584 585 586 587 588 589 590 591 592 593 594 595 596 597 598 599 590 591 592 593 594 595 596 597 598 599 600 601 602 603 604 605 606 607 608 609 610 611 612 613 614 615 616 617 618 619 620 621 622 623 624 625 626 627 628 629 630 631 632 633 634 635 636 637 638 639 640 641 642 643 644 645 646 647 648 649 640 641 642 643 644 645 646 647 648 649 650 651 652 653 654 655 656 657 658 659 660 661 662 663 664 665 666 667 668 669 660 661 662 663 664 665 666 667 668 669 670 671 672 673 674 675 676 677 678 679 680 681 682 683 684 685 686 687 688 689 680 681 682 683 684 685 686 687 688 689 690 691 692 693 694 695 696 697 698 699 690 691 692 693 694 695 696 697 698 699 700 701 702 703 704 705 706 707 708 709 710 711 712 713 714 715 716 717 718 719 720 721 722 723 724 725 726 727 728 729 730 731 732 733 734 735 736 737 738 739 740 741 742 743 744 745 746 747 748 749 740 741 742 743 744 745 746 747 748 749 750 751 752 753 754 755 756 757 758 759 760 761 762 763 764 765 766 767 768 769 760 761 762 763 764 765 766 767 768 769 770 771 772 773 774 775 776 777 778 779 780 781 782 783 784 785 786 787 788 789 780 781 782 783 784 785 786 787 788 789 790 791 792 793 794 795 796 797 798 799 790 791 792 793 794 795 796 797 798 799 800 801 802 803 804 805 806 807 808 809 810 811 812 813 814 815 816 817 818 819 820 821 822 823 824 825 826 827 828 829 830 831 832 833 834 835 836 837 838 839 840 841 842 843 844 845 846 847 848 849 840 841 842 843 844 845 846 847 848 849 850 851 852 853 854 855 856 857 858 859 860 861 862 863 864 865 866 867 868 869 860 861 862 863 864 865 866 867 868 869 870 871 872 873 874 875 876 877 878 879 880 881 882 883 884 885 886 887 888 889 880 881 882 883 884 885 886 887 888 889 890 891 892 893 894 895 896 897 898 899 890 891 892 893 894 895 896 897 898 899 900 901 902 903 904 905 906 907 908 909 910 911 912 913 914 915 916 917 918 919 920 921 922 923 924 925 926 927 928 929 930 931 932 933 934 935 936 937 938 939 940 941 942 943 944 945 946 947 948 949 940 941 942 943 944 945 946 947 948 949 950 951 952 953 954 955 956 957 958 959 960 961 962 963 964 965 966 967 968 969 960 961 962 963 964 965 966 967 968 969 970 971 972 973 974 975 976 977 978 979 980 981 982 983 984 985 986 987 988 989 980 981 982 983 984 985 986 987 988 989 990 991 992 993 994 995 996 997 998 999 990 991 992 993 994 995 996 997 998 999 1000 1001 1002 1003 1004 1005 1006 1007 1008 1009 10010 10011 10012 10013 10014 10015 10016 10017 10018 10019 10020 10021 10022 10023 10024 10025 10026 10027 10028 10029 10030 10031 10032 10033 10034 10035 10036 10037 10038 10039 10040 10041 10042 10043 10044 10045 10046 10047 10048 10049 10050 10051 10052 10053 10054 10055 10056 10057 10058 10059 10060 10061 10062 10063 10064 10065 10066 10067 10068 10069 10070 10071 10072 10073 10074 10075 10076 10077 10078 10079 10080 10081 10082 10083 10084 10085 10086 10087 10088 10089 10090 10091 10092 10093 10094 10095 10096 10097 10098 10099 100100 100101 100102 100103 100104 100105 100106 100107 100108 100109 100110 100111 100112 100113 100114 100115 100116 100117 100118 100119 100120 100121 100122 100123 100124 100125 100126 100127 100128 100129 100130 100131 100132 100133 100134 100135 100136 100137 100138 100139 100140 100141 100142 100143 100144 100145 100146 100147 100148 100149 100150 100151 100152 100153 100154 100155 100156 100157 100158 100159 100160 100161 100162 100163 100164 100165 100166 100167 100168 100169 100170 100171 100172 100173 100174 100175 100176 100177 100178 100179 100180 100181 100182 100183 100184 100185 100186 100187 100188 100189 100190 100191 100192 100193 100194 100195 100196 100197 100198 100199 100200 100201 100202 100203 100204 100205 100206 100207 100208 100209 100210 100211 100212 100213 100214 100215 100216 100217 100218 100219 100220 100221 100222 100223 100224 100225 100226 100227 100228 100229 100230 100231 100232 100233 100234 100235 100236 100237 100238 100239 100240 100241 100242 100243 100244 100245 100246 100247 100248 100249 100250 100251 100252 100253 100254 100255 100256 100257 100258 100259 100260 100261 100262 100263 100264 100265 100266 100267 100268 100269 100270 100271 100272 100273 100274 100275 100276 100277 100278 100279 100280 100281 100282 100283 100284 100285 100286 100287 100288 100289 100290 100291 100292 100293 100294 100295 100296 100297 100298 100299 100300 100301 100302 100303 100304 100305 100306 100307 100308 100309 100310 100311 100312 100313 100314 100315 100316 100317 100318 100319 100320 100321 100322 100323 100324 100325 100326 100327 100328 100329 100330 100331 100332 100333 100334 100335 100336 100337 100338 100339 100340 100341 100342 100343 100344 100345 100346 100347 100348 100349 100350 100351 100352 100353 100354 100355 100356 100357 100358 100359 100360 100361 100362 100363 100364 100365 100366 100367 100368 100369 100370 100371 100372 100373 100374 100375 100376 100377 100378 100379 100380 100381 100382 100383 100384 100385 100386 100387 100388 100389 100390 100391 100392 100393 100394 100395 100396 100397 100398 100399 100400 100401 100402 100403 100404 100405 100406 100407 100408 100409 100410 100411 100412 100413 100414 100415 100416 100417 100418 100419 100420 100421 100422 100423 100424 100425 100426 100427 100428 100429 100430 100431 100432 100433 100434 100435 100436 100437 100438 100439 100440 100441 100442 100443 100444 100445 100446 100447 100448 100449 100450 100451 100452 100453 100454 100455 100456 100457 100458 100459 100460 100461 100462 100463 100464 100465 100466 100467 100468 100469 100470 100471 100472 100473 100474 100475 100476 100477 100478 100479 100480 100481 100482 100483 100484 100485 100486 100487 100488 100489 100490 100491 100492 100493 100494 100495 100496 100497 100498 100499 100500 100501 100502 100503 100504 100505 100506 100507 100508 100509 100510 100511 100512 100513 100514 100515 100516 100517 100518 100519 100520 100521 100522 100523 100524 100525 100526 100527 100528 100529 100530 100531 100532 100533 100534 100535 100536 100537 100538 100539 100540 100541 100542 100543 100544 100545 100546 100547 100548 100549 100550 100551 100552 100553 100554 100555 100556 100557 100558 100559 100560 100561 100562 100563 100564 100565 100566 100567 100568 100569 100570 100571 100572 100573 100574 100575 100576 100577 100578 100579 100580 100581 100582 100583 100584 100585 100586 100587 100588 100589 100590 100591 100592 100593 100594 100595 100596 100597 100598 100599 100600 100601 100602 100603 100604 100605 100606 100607 100608 100609 100610 100611 100612 100613 100614 100615 100616 100617 100618 100619 100620 100621 100622 100623 100624 100625 100626 100627 100628 100629 100630 100631 100632 100633 100634 100635 100636 100637 100638 100639 100640 100641 100642 100643 100644 100645 100646 100647 100648 100649 100650 100651 100652 100653 100654 100655 100656 100657 100658 100659 100660 100661 100662 100663 100664 100665 100666 100667 100668 100669 100670 100671 100672 100673 100674 100675 100676 100677 100678 100679 100680 100681 100682 100683 100684 100685 100686 100687 100688<br				

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